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Description

This invention relates to two-part systems of making filled methacrylate-functional resin compositions, methods for making them and dental use of the systems as defined in the claims.

5 Over the years many dental composites have been introduced, each composite possessing certain physical properties. However, substantially all of these dental composites can be categorized into two main groups, self-cured materials and light-cured materials.

The self-cured composites have involved free radical polymerization initiated by benzoyl peroxide (or another suitable peroxide) and accelerated, typically by a tertiary amine such as N,N-dimethyl-p-toluidine.
10 The curing agents must be stored separately from the resin they are to cure, and they are mixed together just before use.

The light-cured composites have involved free radical polymerization initiated by the photoexcitation of light-sensitive compounds by ultraviolet or visible light. They are single-component systems, typically pastes, stored in opaque containers until the time of cure. Some of the photoinitiators that have been
15 employed are the benzoin ethers, benzil ketals, dialkoxyacetophenones, benzophenones, thioxanthenes, and hydroxyalkylphenones.

In the practice of dentistry, some tooth repairs have been better achieved by self-cured composites and some have been better achieved by light-cured composites. While many factors have helped to determine whether a dentist would or should choose a self-cured material or a light-cured material, the prime factors
20 have been working time, setting time, and the architecture of the cavity preparation.

The light-cured composites, combined with special high-lumen lighting units employing fiber optics, have offered variable working times and fast "snap" sets. Setting can take between ten and forty seconds in many instances. However, the use of light-cured composites has been limited by the depth of the repair and the ease of light penetration. Relatively unobstructed, clean, shallow repair surfaces have been
25 required. Visible-light-cured materials have helped in solving some of the limitations caused by repair depth, by roughly doubling the depths at which cure is effective as compared to ultra-violet light-cured material. Also, many dentists have felt more comfortable using a visible, as opposed to an ultra-violet, activating light source.

The amount of cure is variable and is a function of exposure to lumens of visible light. These facts
30 result in extremely dangerous situations in many dental restorations; because most dentists do not realize this deficiency, because light-cured systems are advertised to be able to be cured through tooth structure. In reality, the situation is, at best, a gradient level of cure obtained in relation to the amount of lumens of light energy available to the restorative resin. That is to say, layers close to the light source undergo greater percent polymerization than the underlying layers. Consequently, the incompletely polymerized restoration
35 may wash out, leak, or fail in adhesion. Yet the surface or bulk of the restoration may appear clinically adequate, even though new secondary decay may be beginning, and, because of its concealment, result in death of the pulp or loss of the tooth.

When a light-cured resin liner is used with a light-cured paste composite at a depth of around 3 mm. or greater, the resin liner may not cure because of insufficient light reaching the resin. Uncured resin liner can
40 cause leaching, pulpal irritation, and loss of adhesion. Heretofore, the resin liner had, therefore, to be polymerized prior to placement of the composite. With this invention, such double cure is unnecessary.

Self-cured systems have offered assurance of polymerization throughout the polymer mass used in any repair surface architecture. However, their use has been limited by manufacturer-determined work times and set times. The peroxide and the accelerator could be adjusted to give widely varying setting times; the
45 quicker the set time, the quicker the placement had to be made. Thus, in order to give enough time for accurate placement, the set times had to be longer than were desirable. Generally, set times have been at least two or three minutes after mix, and placement has had to be completed within forty-five seconds after mix. This had made dentists work somewhat faster than was desirable for many placements, and even then the patient had to be immobilized longer than was desirable before the composition set.

50 This invention overcomes the deficiencies of light-cured systems, while preserving their functional benefits. It also overcomes the deficiencies of the self-cured systems by enabling quicker set times coupled with longer placement times, if desired.

The system of this invention thus offers the best properties of both types of curing systems without suffering from the limitations of either, and therefore it significantly advances the practice of dentistry and
55 the science of dental materials.

The system of the present invention can be in a powder-liquid, paste-paste, paste-powder, or gel-powder form, so that there is no loss in versatility of possible embodiments.

Similar problems occur with porcelain repair systems in general, not only in dental uses, but for

repairing such porcelain articles as bathtubs, and the invention solves these problems also.

Summary of the Invention

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This invention comprises a composite system combining a small amount of peroxide curing agent, free from accelerator, with certain photoinitiator systems called exciplexes. A two-component system is required, with mixture just before use. Conveniently, the resin and its exciplex members can be stored in opaque (preferably black) containers as one component, with or without some of the filler. The peroxide is stored in
 10 a separate component, including much or all of the filler-colorant, in a container which need not be opaque. The two components are mixed just prior to application, and there is a wide latitude of mixing time, because no accelerator is used. The curing effect of the peroxide in the resin is quite slow, while the exposure of the resin and photoinitiator exciplex members in ordinary light--whether daylight or artificial light--will not result in substantial curing. The time for placement is not critical, because neither the photoinitiator exciplex nor
 15 the peroxide causes quick curing at this stage. After placement, a high-lumen light source is used with a fiber-optics bundle to effect rapid cure (typically, ten to forty seconds) down to a substantial depth. If the cavity being filled is deeper than that depth, or if some of the placed material has been shaded from the light or not adequately illuminated, the light alone does not effect sufficient cure. However, the cured deposit covering the uncured material holds the uncured material in place, and the peroxide has been found
 20 to effect cure of the uncured material in about an hour, and usually in about half that long.

To explain exciplexes: as in photoinitiator systems generally, absorption of light by the ketone group of some photoinitiators results in promotion of the photoinitiator to a chemically reactive excited state; alpha-cleavage results, and free radicals are formed. "In the case of appropriate donor/acceptor systems, interaction between an electronically excited molecule and a ground-state molecule of another type may
 25 form an excited-state complex, termed an 'exciplex'." Roffey, C. G., Photopolymerization of Surface Coatings, p. 70, John Wiley and Sons, Ltd., New York, 1982.

The incorporation of a suitable peroxide, preferably benzoyl peroxide, with the photoinitiated composite system has a synergistic effect on the free-radical polymerization, resulting in uniform cure without limitation after exposure to the activating light source. The peroxide content is preferably 0.05% to 0.3% of the total
 30 composition.

The exciplex photoinitiators of this invention are a combination of (1) either 2,3-bornanedione or benzil and (2) either ethyl-4-dimethyl-amino-benzoate or ethyl-2-dimethyl-amino-benzoate. The amount should be enough to initiate polymerization in the selected resin and complete it in depth within half a minute when the filled-resin composition is exposed to a visible-light output of at least 53800 lx (5,000 foot candles). The
 35 peroxide should be present in amount sufficient to complete, within about an hour, the resin's polymerization, where it is not completed by the photoinitiator-derived action, as where the light never reaches the resin in the needed amount.

Thus, suitable photoinitiators for this invention are the following exciplex-forming photoinitiators:

- 2,3-Bornanedione with ethyl-4-dimethyl-amino-benzoate
- 40 2,3-Bornanedione with ethyl-2-dimethyl-amino-benzoate
- Benzil with ethyl-4-dimethyl-amino-benzoate
- Benzil with ethyl-2-dimethyl-amino-benzoate.

There are, of course, many other compounds capable of photoinitiation. Many of these are taught in U.S. 4,222,835, to Dixon. However, Dixon's formulations were intended for industrial fabrication, whereas the
 45 present invention involves formulations which can be left in the human mouth for many years. Consequently, compounds which are known or are suspected to be toxic, carcinogenic, teratogenic or mutagenic are not considered.

The present invention provides a much deeper cure than do light-cured composites and obtains a much more uniform degree of cure than do such systems. It obtains a certainty of cure under overhangs, as
 50 opposed to prior-art light-cured composites, and a more reliable cure through tooth structure than the prior-art light-cured composites. It provides more uniformity of cure, regardless of exposure time or intensity. It provides better adhesion to the teeth or to substrates such as porcelain as used in dentistry and in plumbing fixtures, apparently due to more complete polymerization. It has a longer shelf-life than self-cured composites. It has better physical properties than most prior-art light-cured composites, especially lower
 55 water absorption.

It does not develop color bodies in composites using chemically active glasses, such as strontium glass, where some curing systems do develop objectionable color. Moreover, the composite, when installed and cured in a dental environment, looks like the tooth, not only in ordinary light but also in ultra-violet light.

In ultra-violet light it fluoresces to substantially the same degree as the tooth itself.

As stated above, the product is made up of two separate formulations, one containing all or much of the material to be cured along with the exciplex photoinitiators. This formulation is kept from light, as in an opaque container. The other formulation contains the peroxide curing agent, preferably along with any ingredient not itself cured thereby, such as the filler-colorants.

Description of Some Preferred Embodiments

10 The binders or resins to be cured comprise substantially all of those currently used in dental composites. These are all methacrylate-functional resins. Typical is ethoxylated bisphenol-A-dimethacrylate. Others include Bis-GMA and the adducts disclosed in Waller's U.S. Patent No. 3,629,187. Mixtures of resins may be used. Waller's adducts are of 2-2'-propane bis [3-(4-phenoxy)-1,2-dihydroxy propane-1-methacrylate] and a mono- or di-isocyanate.

15 The curing agents, as said, are of two types: peroxides and photoinitiators. A suitable and preferred peroxide is benzoyl peroxide. Some other peroxides are either inoperable or have dangerous toxic side effects.

The photoinitiators are in the same component as the resin, the resin- photo-initiator exciplex components mixture being kept in opaque containers until use. The peroxide is ordinarily kept separate from the resin, usually with or upon the filler-colorant or most of the filler-colorant. In paste-paste systems, some of the resin may be in the same component as the peroxide.

The suitable exciplex-forming photoinitiators are the following:

2,3-Bornanedione with ethyl-4-dimethyl-amino-benzoate

2,3-Bornanedione with ethyl-2-dimethyl- amino-benzoate

25 Benzil with ethyl-4-dimethyl-amino-benzoate

Benzil with ethyl-2-dimethyl-amino-benzoate.

To the best of our knowledge, no one has previously suggested that the combination of any of these light-curing exciplex photoinitiators with any peroxide could bring about better curing of these dental resins. Likewise, it is not ordinary to utilize peroxide in such small amounts as those utilized in this invention to initiate polymerization of these resins. Furthermore, peroxide curing agents are conventionally employed with accelerators, and no accelerator is used here. Consequently, the results obtained by this invention were totally unexpected.

Practically all inert filler-colorants currently used or usable in dental composites are usable herein. Preferably, they are neither too coarse nor too fine. The compositions employed in this invention may contain at least 10% by weight and up to 90% by weight, and preferably 70-80% by weight, of a finely divided, inert inorganic filler-colorant. The filler-colorant, which may be in the form of spheres, platelets, fibers, whiskers, or particles of any regular or irregular shape and which preferably is transparent or translucent, may comprise for example, apatite, soda glass, barium glass, strontium glass, borosilicate glass, silica, fumed silica, flint silica, alumina, quartz or lithium aluminum silicate. Mixtures of more than one filler-colorant may be used. The particle size of the filler-colorant may range from 0.005 to 0.5 microns in the case of microfine silica, to not greater than 500 μ m (microns) in the case of irregularly shaped particles. Further, a range of particles sizes may be used. Where the filler-colorant is in the form of fibers, the maximum dimension of the fibers preferably is not greater than 110 μ m (microns). On the other hand, where the filler-colorant is in the form of spheres or platelets or is irregularly shaped, the maximum dimension of the particles preferably is not greater than 350 μ m(microns).

The identity of the filler-colorant is not critical, but barium-containing glass (hereinafter called "barium glass"), strontium-containing glass (hereinafter called "strontium glass"), lithium aluminum silicate, flint silica, and fumed silica are excellent fillers and mixtures of these are usually preferable to the use of just one of them. For example, lithium aluminum silicate has a negative heat coefficient of expansion, giving lower overall thermal dimensional changes to the composite. Barium and strontium glass impart opacity to X-rays. Flint silica imparts tooth-like color, and fumed silica adjusts viscosity and improves polishability.

One example of barium glass is Ray-Sorb T-2000, a product of Kimble Division of Owens-Illinois Glass Company. The same company makes Ray-Sorb T-4000, an example of strontium glass.

Preferably, the peroxide is dispersed on the filler-colorant powder, or by being dissolved in a suitable solvent, is sprayed on the filler-colorant powder, and the solvent evaporated. Preferably, the peroxide is deposited in combination with a silane, such as gamma-methacryloxy propyl trimethoxy silane (sold by Union Carbide as A-174 silane), which is used to improve bonding between the filler and the resin. The benzoyl peroxide and the silane may be dissolved in methylene chloride, chloroform, ether, or acetone, for

example. Then a slurry is made with the powdered filler-colorant; the solvent is stripped off, leaving the silane and the peroxide deposited on the dry powder filler-colorant.

Glacial acetic acid is often used, in very small amounts, because the hydrolysis reaction which attaches the silane molecule to the filler-colorant particle is carried out most effectively at a pH slightly less than neutral.

Butylated hydroxytoluene is sometimes used in order to scavenge small amounts of free radicals which can form during extended shelf storage.

The invention can assume the following forms: a powder-liquid form, a paste-paste form, a paste-powder form, and a gel-powder form. These forms will be considered in order.

Powder-liquid systems(d)

In general, the powder in this form comprises a suitable filler-colorant material, a suitable silane, such as gamma-methacryloxy propyl trimethoxy silane, and a suitable peroxide curing agent such as benzoyl peroxide. Preferably, these ingredients are in the following approximate range of proportions by weight:

Powder

<u>Ingredients</u>	<u>Percentage by Weight</u>
Filler-colorant	99.85 to 97.70%
Silane	0.10 to 1.55%
Peroxide curing agent	0.05 to 0.70%
Glacial acetic acid	0.00 to 0.05%

As stated above, the filler-colorant may be a mixture of some or several of the filler-colorants listed above, or it may be just one type of filler.

Liquid

<u>Ingredients</u>	<u>Percentage by Weight</u>
Resin	99.3 to 81.95%
Photoinitiator exciplex	0.7 to 18%
Butylated hydroxy toluene	0.00 to 0.05%

The formulae may be, further generalized in a somewhat more specific manner as follows: it being understood that the various types of ingredients (e.g., filler-colorant and resin) will be used in quantities that will total to the amounts just spelled out above:

Preferably, the liquid component consists essentially of a methacrylate-functional resin in an amount of 96-84% by weight and the photoinitiator incorporates as one ingredient either ethyl-4-dimethyl-amino-benzoate or ethyl-2-dimethyl-amino-benzoate in an amount of 0.7 to 10% by weight of the liquid component, the other ingredient being either 2,3-bornanedione or benzil and present in an amount of 0.01-8% by weight

Powder:

	<u>Ingredients</u>	<u>Percentage by Weight</u>	
5	Barium glass	0	to 30 (more specifically 23-30%)
	Lithium aluminum silicate	0	to 99.85 (more specifically 54-70%)
	Flint silica	0	to 10 (more specifically 1-10%)
	Borosilicate glass	0	to 99.85
10	Custer feldspar	0	to 10.00
	Fumed synthetic silica	0	to 99.85
	Quartz	0	to 99.85
	Titanium dioxide	0	to 0.15
15	Tinting agents		
	(e.g., iron oxides)	0	to 5
	A-174 Silane	0.1	to 1.55
	Peroxide curing agent	0.05	to 0.70
20	Glacial acetic acid	0	to 0.05 (more specifically 0.001-0.05%)

Liquid

	<u>Ingredients</u>	<u>Percentage by Weight</u>	
25	Bis-GMA	0	to 80
	Ethoxylated bisphenol-A-		
30	dimethacrylate	0	to 99.3 (more specifically 82-99.3%)
	Ethylene glycol		
	dimethacrylate	0	to 60
	Diethylene glycol		
35	dimethacrylate	0	to 60
	Triethylene glycol		
	dimethacrylate	0	to 60
	Polyethylene glycol		
40	dimethacrylate	0	to 60
	Photoinitiator (one or		
	more from the exciplex		
	list above)	0.7	to 18
45	Butylated hydroxy toluene	0	to 0.05 (more specifically 0.02%)

More specifically, the resin is a mixture of 60-84% ethoxylated bisphenol-A-dimethacrylate and 40-16% triethylene glycol dimethacrylate or a mixture comprising 55% BIS-GMA and 36% triethylene glycol dimethacrylate. The photoinitiator may comprise 2,3-bornanedione in amounts of 0.02-0.2%.

Tinting agents are used to impart a more tooth-like color. Red and yellow iron oxides are usually employed.

Storage life for each mixture is very long, no deterioration having been noticed so far over a period of two and one-half years. The powder and the liquid are mixed together in a ratio of weight from 1:1 to 4:1, preferably 2:1 to 3.5:1 powder to liquid, just before they are needed. Mixing may be accomplished on a paper mixing pad, with a plastic instrument. Mixing may be done under normal room lighting conditions, as found in the dental operator, illumination typically varying in intensity from 86 to 1076 lx (80 to 100 foot candles). Under these conditions, the paste begins to gel after 10 to 30 minutes, depending on the

particular formulations and illuminations.

When it is desired to initiate curing, the mixed material is exposed to the output from a dental visible light curing unit. For all examples cited herein, a Visar light curing unit, marketed by Den-Mat, Inc., Santa Maria, California, was used. This unit utilizes a type EKE or EJV quartz-halogen light bulb, operating at 21 VAC. The light is transmitted to the work site by a flexible fiber-optic bundle, 6.35mm (1/4 inch) in diameter by 1.22m (four feet) in length. Other units are available from other manufacturers. All are similar in principle and results. Results of these examples would be expected to differ only in degree if other units were used. The output of the Visar unit used is 180×10^4 Candella per square meter, giving illumination of about 215,200 lx (20,000 foot candles) on the material being cured. Satisfactory operability can be achieved with 53800 lx (5,000 foot candles).

Under these conditions, the material cures in from 10 seconds to 30 seconds, with a cured depth of from 0.60 to 5.60 mm. Upon further standing, that is, from 5 minutes to 35 minutes, the material exhibits a cure depth of greater than 12 mm. It shows a tensile strength, measured by the diametral method on samples 6 mm diameter by 3 mm high, of between 330.95 and 482.64.10⁵Pa (4800 psi and 7000 psi). A popular prior-art, light-cured dental composite, when tested in identical fashion, showed a cure depth of 3.05 mm immediately after exposure to the curing light, but this cure depth did not increase over a period of 16 hours after cure, and its diametral tensile strength was only 140.10⁵Pa (2030 psi).

20 EXAMPLE 1

Powder-Liquid System

Powder:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Barium glass	28.63%
Lithium aluminum silicate	67.84%
Flint silica	2.84%
Benzoyl peroxide	0.20%
A-174 silane	0.47%
Glacial acetic acid	0.02%

A-174 silane is a Union Carbide product, chemically gamma-methacryloxy propyl trimethoxy silane. The barium glass may be Ray-Sorb T-2000, a product of Kimble Division of Owens-Illinois Glass Company or may be barium aluminum silicate.

Liquid

<u>Ingredients</u>	<u>Percentage by Weight</u>
Ethoxylated bisphenol-A-	
dimethacrylate	95.53%
2,3-Bornanediol	0.17%
Ethyl-4-dimethylamino-	
benzoate	4.30%

The powder and the liquid were mixed together, preferably in a ratio by weight of 2:1 to 3.5:1, powder

to liquid, just before they were needed. Mixing took twenty seconds. The mixtures are preferably applied within five minutes. The setting time was twenty minutes when not exposed to a dental curing light, but was less than thirty seconds on exposure to a dental curing light. The result was a hard filling.

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EXAMPLE 2

Hardness comparisons with some prior-art systems:

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A disk of a commercially available light-curable dental composite was prepared, 20 mm diameter by 1 mm thick. One-half of this disk was shaded with aluminum foil, and the disk then was placed under a photoflood lamp for 15 minutes. The sample was removed from under the lamp, the foil removed from the sample, and Barcol hardness measured on both the shaded and unshaded halves. The unshaded half showed a Barcol hardness of 82, while the shaded side had a Barcol hardness reading of less than 1. This same experiment was performed on a disk made of the mixed but uncured material of Example 1, and both sides of this disk showed a Barcol hardness of 92.

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EXAMPLE 3

Comparison of degree of cure:

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A series of tests was performed on several commercially-available light-curing composites to determine the degree of cure of the resin matrix. Testing was accomplished by preparing duplicate samples, 1 mm thick by 40 mm in diameter. These samples were cured by exposing them to a photoflood lamp for 30 minutes, and then they were placed in 37° C. water for 24 hours. The samples were then dried, and placed in a desiccator and weighted daily until constant weight (+ 0.5 mg.) was achieved. The samples were then granulated, placed in a glass thimble and extracted for 12 hours in a Soxhlett extraction apparatus with methylene chloride. After extraction, the samples were weighted and the weight loss converted to percent uncured monomer removed.

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When two popular commercially-available light-cured dental composites were tested in this manner, the cured product contained 3.08% and 5.26% extractables, representative of the amount of uncured monomer.

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The material of Example 1 of this invention, when tested in the same manner, contained only 1.87% extractables, showing a much higher degree of cure.

EXAMPLE 4

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Comparison of degree of water sorption:

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A series of three light-cured dental restoratives were tested in order to determine the degree of water sorption. Samples were in duplicate, and were configured and tested in accordance with American Dental Association Specification No. 27.

Two popular commercially-available light-cured dental restoratives were found to have water sorption values of 1.05 and 0.95 mg/cm², respectively. The material of Example 1 gave a value of only 0.86 mg/cm².

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EXAMPLE 5

Powder-liquid system of porcelain repair:

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The powder-liquid system of Example 1 was tested as a porcelain repair material, as described in U.S. Patent No. 4,117,595.

A commercially available material marketed to practice the above-mentioned patent had test results of

739.10⁵ Pa (2015 psi) bond strength (average of 5 samples) when tested 7 days after preparation, being stored meantime in water at 37°C.

The material of Example 1, when tested in the same fashion, with the same test equipment, gave results of 765.5 10⁵ Pa (2400 psi) bond strength or 19.1% higher.

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EXAMPLE 6

10 Comparison with a conventional powder-liquid system (using larger amounts of benzoyl peroxide than this system):

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Powder:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Strontium glass	
(Ray-sorb T-4000)	95.69%
A-174 Silane	1.44%
Benzoyl peroxide	2.87%

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Liquid:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Ethoxylated bisphenol-A-	
dimethacrylate	77.21%
Triethylene glycol	
dimethacrylate	19.31%
1-Hydroxy-4-methoxy-	
benzophenone	1.93%
Butylated hydroxytoluene	0.05%
N,N-2-hydroxyethyl-p-	
toluidine	1.50%.

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45 The powder and liquid were mixed in a weight ratio of 3:1 of powder to liquid and cured properly. However, a bright green color was formed on curing. The mixture was repeated after acid-washing the strontium glass, but the green color persisted. The mixture was again repeated using N,N-3,5-tetramethylaniline as a substitute for the N,N-2-hydroxyethyl-p-toluidine. Again the green color developed.

The mixture was repeated once again using N,N-dimethyl-p-toluidine as activator instead of the N,N-2-hydroxyethyl-p-toluidine. This time the green color did not develop, but the curing characteristics of the

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Then the experiment was repeated, using the following powder and liquid:

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Powder:IngredientsPercentage by Weight

5	Strontium glass	
	(Ray-sorb T-4000)	98.300%
	A-174 Silane	1.475%
	Benzoyl peroxide	0.200%
10	Acetic acid	0.025%

Liquid:IngredientsPercentage by Weight

15	Ethoxylated bisphenol-A-	
	dimethacrylate	76.41%
20	Triethylene glycol	
	dimethacrylate	19.10%
	2,3-Bornanediol	0.17%
	Ethyl 4-dimethyl amino	
25	benzoate	4.30%
	Butylated hydroxytoluene	0.02%

30 No color developed, the material cured satisfactorily under the output from a Visar dental light curing unit, and exhibited a depth of cure of 5.20 mm immediately after exposure to the light, and 12 mm depth of cure after 30 minutes. Diametral tensile strength was 473.67.10⁵ Pa (6000 psi).

35 EXAMPLE 7

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Powder-Liquid SystemPowder:IngredientsPercentage by Weight

Barium glass	28.63%
Lithium aluminum silicate	66.80%
Flint silica	2.84%
Benzoyl peroxide	0.20%
A-174 silane	1.51%
Glacial acetic acid	0.02%

LiquidIngredientsPercentage by Weight

Ethoxylated bisphenol-A- dimethacrylate	95.53%
2,3-Bornanedione	0.17%
Ethyl-4-dimethylamino- benzoate	4.30%

Again, the powder and liquid were mixed together in a weight ratios varying from 2:1 to 3.5:1, powder to liquid. Curing time was 30 seconds with a depth of 5.50 mm when exposed to a visible light dental curing unit. Diametral tensile strength was 448.16×10^5 Pa (6500 psi). The paste had a workable time of 30 minutes under normal room fluorescent lighting.

EXAMPLE 8

Powder-Liquid SystemPowder:IngredientsPercentage by Weight

Lithium aluminum silicate	66.80%
Barium glass	28.63%
Flint silica	2.84%
Benzoyl peroxide	0.20%
A-174 silane	1.51%
Glacial acetic acid	0.02%

LiquidIngredientsPercentage by Weight

Bis-GMA, i.e.,	
2,2'-propane-bis-	
[3-(4-phenoxy)-1,2-di-	
hydroxy propane-1-	
methacrylate]	57.40%
Triethylene glycol	
dimethacrylate	37.94
2,3-Bornanediol	0.02%
Ethyl-4-dimethylamino-	
benzoate	4.64%

Three parts of the powder and one part of the liquid were mixed together to form a paste. This paste, when exposed to a visible light dental curing unit for 30 seconds, cured to a depth of 5.40 mm. Under normal room fluorescent lighting, the paste had a workable time of approximately 20 minutes. The diametral tensile strength was $475.74 \times 10^5 \text{ Pa}$ (6900 psi).

EXAMPLE 9

Powder-Liquid SystemPowder:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Lithium aluminum silicate	66.80%
Barium glass	28.63%
Flint silica	2.84%
Benzoyl peroxide	0.20%
A-174 silane	1.51%
Glacial acetic acid	0.02%

Liquid

<u>Ingredients</u>	<u>Percentage by Weight</u>
Ethoxylated bisphenol-A-dimethacrylate	75.98%
Triethylene glycol dimethacrylate	19.36%
2,3-Bornanedione	0.02%
Ethyl-4-dimethylamino-benzoate	4.64%

Three parts of the powder and one part of the liquid were mixed together to form a paste. This paste, when exposed to the output from a Visar dental visible light curing unit for 30 seconds, cured to a depth of 5.30 mm. When left exposed to room fluorescent lighting, the paste had a working time of 40 minutes and a diametral tensile strength of $478.5 \times 10^5 \text{ Pa}$ (6940 psi).

EXAMPLE 10A comparison of curing of various powder/liquid systems utilizing different exciplex-forming photoinitiators

A series of resin blends was prepared, all as indicated below as resins A-N, where all the percentages of ingredients are given by weight. Also a standard blend of powder was prepared. Benzoyl peroxide was added to the powder in different levels. The resultant powders were mixed with the resin blends and exposed to the output from a Visar dental light curing unit for 30 seconds, and the depth of cure measurement was taken.

As controls resin blends were made without one or all of the exciplex members.

On some of these samples, glass tubes 12 mm long were filled with the test material, and were wrapped with black vinyl tape to exclude light for 30 seconds, then the time was measured until the material at the opposite end of the tube was cured. This test will be referred to as the "Infinite Depth of Cure Test" in the following text.

As a control, a popular commercially available light-cured composite was tested in the same manner. It initially cured in 30 seconds to a depth of 3.05 mm, and there was no increase in cure depth when measured after 16 hours.

Standard Blend of Powder

5	Barium glass	29.54%
	Lithium aluminum silicate	68.96%
	A-174 silane	1.48%
10	Glacial acetic acid	0.02%

Resin A (comparative resin):

15	Ethoxylated bisphenol-A-	
	dimethacrylate	100.00%

20 Resin A was mixed in a ratio of 1:2 with a powder blend containing 0.61% added benzoyl peroxide. No cure was observed.

Resin B:

25	Ethoxylated bisphenol-A-	
	dimethacrylate	95.53%
	2,3-Bornanediol	0.17%
30	Ethyl-4-dimethylamino-	
	benzoate	4.30%

35 Resin B was mixed in a ratio of 1:3 with powder blends containing 0.20 and 0.22% added benzoyl peroxide. The cure depths observed were both 5.50 mm. The time in minutes after light exposure for "infinite cure" of the blend made with the 0.22% added peroxide was 30.

Resin C: (comparative resin):

40	Ethoxylated bisphenol-A-	
	dimethacrylate	91.70%
	Benzoin methyl ether	8.30%

45 Resin C was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 1.32 mm. There was no subsequent increase in cure depth.

Resin D: (comparative resin):

50	Ethoxylated bisphenol-A-	
	dimethacrylate	84.60%
	Benzoin methyl ether	7.70%
55	Ethyl-4-dimethylamino-	
	benzoate	7.70%

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Resin D was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 2.55 mm. The time in minutes after light exposure for "infinite cure" of the blend was 60.

5	Resin E (comparative resin):	
	Ethoxylated bisphenol-A-	
	dimethacrylate	82.30%
	Benzoin methyl ether	7.70%
10	Ethyl-2-dimethylamino-	
	benzoate	10.00

15 Resin E was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 2.65 mm. The time in minutes after light exposure for "infinite cure" of the blend was 45.

	Resin F (comparative resin):	
20	Ethoxylated bisphenol-A-	
	dimethacrylate	86.60%
	Benzoin methyl ether	3.40%
	Ethyl-2-dimethylamino-	
25	benzoate	10.00

30 Resin F was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 2.74 mm. The time in minutes after light exposure for "infinite cure" of the blend was 60.

	Resin G (comparative resin):	
	Ethoxylated bisphenol-A-	
35	dimethacrylate	88.80%
	Benzoin methyl ether	3.50%
	Ethyl-4-dimethylamino-	
40	benzoate	7.70%

45 Resin G was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 3.53 mm. The time in minutes after light exposure for "infinite cure" of the blend was 50.

	Resin H (comparative resin):	
	Ethoxylated bisphenol-A-	
	dimethacrylate	91.70%
50	Benzil	8.30%

55 Resin H was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 4.06 mm. There was no subsequent increase in the depth of cure.

Resin I:

5	Ethoxylated bisphenol-A-	
	dimethacrylate	84.60%
	Benzil	7.70%
10	Ethyl-4-dimethylamino-	
	benzoate	7.70%

Resin I was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 4.84 mm. The time in minutes after light exposure for "infinite cure" of the blend was 25.

Resin J:

	Ethoxylated bisphenol-A-	
20	dimethacrylate	84.60%
	Benzil	7.70%
	Ethyl-2-dimethylamino-	
25	benzoate	7.70%

Resin J was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 5.02 mm. The time in minutes after light exposure for "infinite cure" of the blend was 25.

Resin K:

	Ethoxylated bisphenol-A-	
	dimethacrylate	91.50%
35	2,3-Bornanedione	0.17%
	Ethyl-2-dimethylamino-	
40	benzoate	8.33%

Resin K was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 5.56 mm. The time in minutes after light exposure for "infinite cure" of the blend was 60.

Resin L (comparative resin):

	Ethoxylated bisphenol-A-	
	dimethacrylate	88.80%
50	Dibenzyl ketone	3.40
	Ethyl-4-dimethylamino-	
55	benzoate	7.80%

Resin L was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 1.87 mm. The time in minutes after light exposure for "infinite cure" of the blend was 45 minutes.

Resin M (comparative resin):

Ethoxylated bisphenol-A- dimethacrylate	86.60%
Dibenzyl ketone	3.40%
Ethyl-2-dimethylamino- benzoate	10.00%

Resin M was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 0.84 mm. The time in minutes after light exposure for "infinite cure" of the blend was 50 minutes.

Resin N (comparative resin):

Ethoxylated bisphenol-A- dimethacrylate	96.60%
Dibenzyl ketone	3.40%

Resin N was mixed in a ratio of 1:3 with a powder blend containing 0.20% added benzoyl peroxide. The cure depth was 1.55 mm. The time in minutes after light exposure for "infinite cure" of the blend was 52 minutes.

Paste-Paste Systems (a)

Some dentists (and perhaps other users) prefer to work with pastes: most of these users also prefer to use equal amounts of the two pastes, so that paste-paste systems are usually formulated to enable use of equal amounts.

In general, the paste-paste system of the present invention may be formulated as follows:

Paste A:

	<u>Ingredients</u>	<u>Percentage by Weight</u>
5	Resin	14 to 39.63
	Filler-colorant	84.68 to 59.46
	Peroxide	0.10 to 0.75
10	A-174 silane	1.21 to 0.06
	Butylated hydroxytoluene	0.01 to 0.10

Paste B:

	<u>Ingredients</u>	<u>Percentage by Weight</u>
20	Resin	14 to 35.43
	Filler-colorant	83.24 to 53.17
	Exciplex forming photoinitiator	1.5 to 3.5
25	A-174 silane	1.21 to 0.05
	Glacial acetic acid.	0.05 to 0.01

Both pastes contain resin and filler material in an amount totaling over 95% thereof by weight of each paste.

30 The two pastes are mixed in equal amounts. Mixing time, working time, and setting time are approximately the same as for the powder-liquid systems, described above, and the results in cure and hardness are approximately the same, too. Again, ordinary room lighting has little curing effect. The resin may be the same in both pastes, as may the filler. The silane is preferably deposited on the filler of both pastes prior to making the pastes. The presence of both resin and peroxide in Paste A seems not to effect

35 a cure nor to affect substantially the storage life.

More specifically considered, the paste-paste system employs the following formulations:

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Paste A:

<u>Ingredients</u>	<u>Percent by Weight</u>	
5	Bis-GMA	0 to 32
	Ethoxylated bisphenol-A-dimethacrylate	0 to 40
	Ethylene glycol dimethacrylate	0 to 24
	Diethylene glycol dimethacrylate	0 to 24
10	Triethylene glycol dimethacrylate	0 to 24
	Polyethylene glycol dimethacrylate	0 to 24
	Barium glass	0 to 25
15	Lithium aluminum silicate	0 to 85
	Flint silica	0 to 8.5
	Borosilicate glass	0 to 85
20	Fumed synthetic silica	0 to 52
	Quartz	0 to 85
	Strontium glass	0 to 85
	Titanium dioxide	0 to 0.13
25	Tinting agents (e.g., iron oxides)	0 to 4
	A-174 Silane	0.06 to 1.21
	Peroxide curing agent	0.10 to 0.75
30	Butylated hydroxy toluene	0.01 to 0.1

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Paste B:

Ingredients	Percent by Weight
Bis-GMA	0 to 32
5 Ethoxylated bisphenol-A-dimethacrylate	0 to 40
Ethylene glycol dimethacrylate	0 to 24
Diethylene glycol dimethacrylate	0 to 24
10 Triethylene glycol dimethacrylate	0 to 24
Polyethylene glycol dimethacrylate	0 to 24
Barium glass	0 to 25
15 Lithium aluminum silicate	0 to 85
Flint silica	0 to 8.5
Borosilicate glass	0 to 85
Fumed synthetic silica	0 to 52
20 Quartz	0 to 85
Strontium glass	0 to 85
Titanium dioxide	0 to 0.13
25 Tinting agents (e.g., iron oxides)	0 to 4
A-174 Silane	0.05 to 1.21
Exciplex-forming-photoinitiator	1.5 to 3.5
30 Glacial acetic acid	0.01 to 0.05

This formulation should be read with the more general one preceding it, to supply the percentages of fillers, resins, and silane needed, along with appropriate amounts of the curing agents. All percentages are by weight.

EXAMPLE 11Paste-Paste SystemPaste A:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Ethoxylated bisphenol-A-dimethacrylate	17.66%
Benzoyl peroxide	0.30%
50 Butylated hydroxytoluene	0.04%
Barium glass	24.25%
Lithium aluminum silicate	56.43%
55 Fumed silica	0.92%
A-174 silane	0.40%

The fumed silica may be Aerosil 200 of Degussa Corp. of Teterboro, New Jersey.

Paste B:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Ethoxylated bisphenol-A-	
dimethacrylate	14.94%
2,3-Bornanedione	0.06%
Ethyl-4-dimethylamino	
benzoate	1.55%
Barium glass	24.394%
Lithium aluminum silicate	56.92%
Fumed silica	0.92%
A-174 silane	1.2%
Glacial acetic acid	0.016%

The two pastes are preferably mixed in equal quantities just before application and are cured by a dental curing light, such as Visar, or equivalent. When so mixed and exposed to a visible light curing unit for 30 seconds, the material cured to a depth of 5.43 mm. The diametral tensile strength was 487.95×10^5 Pa (6990 psi).

EXAMPLE 12

Paste A:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Ethoxylated bisphenol-A-	
dimethacrylate	17.66%
Benzoyl peroxide	0.30%
Butylated hydroxytoluene	0.04%
Strontium glass	79.88%
Fumed silica	0.92%
A-174 silane	1.20%

The strontium glass may be Ray-sorb T-4000 of Kimble Division of Owens-Illinois.

Paste B:IngredientsPercentage by Weight

5	Ethoxylated bisphenol-A-	
	dimethacrylate	14.94%
	2,3-Bornanediol	0.06%
10	Ethyl-4-dimethylamino	
	benzoate	1.55%
	Strontium glass	81.3284%
	Fumed silica	0.92%
15	A-174 silane	1.20%
	Glacial acetic acid	0.0016%

20 Equal or substantially equal amounts of pastes A and B are mixed together just before use. When so mixed and exposed to a visible light curing unit for 30 seconds, the material cured to a depth of 5.50 mm. The diametral tensile strength was 330.26×10^5 Pa (4790 psi).

25 EXAMPLE 13

The pastes from Examples 11 and 12, mixed in equal parts, were exposed to the output from a Visar dental curing unit for 30 seconds. The samples were tested to determine the time required to achieve a 12 mm (or "infinite") depth of cure. The samples were tested as described previously. Pastes A and B of Example 11 when mixed together obtained "infinite" cure in 35 minutes. Pastes A and B of examples 12 when mixed together obtained "infinite" cure in 35 minutes.

Paste-Powder Systems (b)

35 A third type of system is somewhat of a blend between the powder-liquid system and the paste-paste system. Here, the powder remains substantially the same as in the powder-liquid system, except that it has a larger percentage of peroxide. However, the paste contains the exciplex-forming members dissolved in a liquid resin, and the filler, suspended therein. This paste material should be stored in a light-free container.
40 Typically, a black polyethylene or polypropylene syringe may be used as the container, as in the paste-paste systems.

The powder is coated with a suitable silane, such as gamma methacryloxy propyl trimethoxy silane, and has benzoyl peroxide dispersed over its surface. This component may be stored in a container suited to dispersing small amounts. A small cylindrical plastic vial with a small orificed dropper tip is preferred.

45 In practice, an amount of the paste is expressed onto a mixing pad, then a very small amount--1/10 to 1/20-- of the powder is mixed in; so the powder has more peroxide in it than in previous systems discussed. The result is that the paste is thickened--a condition desired by some dentists--and also that depth of cure and cure efficiency are improved.

A general formulation may be expressed as follows:

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Paste:

	<u>Ingredients</u>	<u>Percentage by Weight</u>
5	Resin	13.00 to 63.4
	Filler-colorant	84.78 to 32.85
	Exciplex-forming photoinitiators	0.78 to 3.70
10	A-174 silane	1.50 to 0.05
	Glacial acetic acid	0.02 to 0.004

15 Powder:

	<u>Ingredients</u>	<u>Percentage by Weight</u>
	Filler-colorant	99.58 to 83.83
20	A-174 silane	0.10 to 6
	Peroxide	0.30 to 10.00
	Glacial acetic acid	0.02 to 0.17

25 The paste comprises the mixture of resin and powdered dental filler in a total amount lying between 96 and 98% by weight of the paste.

The exciplex is preferably made up of

(a) 2,3-bornanedione in an amount of 0.03 to 0.06% by weight of said paste and,

30 (b) either ethyl-4-dimethyl-amino-benzoate or ethyl-2-dimethyl-amino-benzoate in an amount of 0.75 to 3.25 by weight of said paste.

More specifically, the resin is a mixture of 13% ethoxylated bisphenol-A-dimethacrylate and 3.25% of triethylene glycol dimethacrylate, both by weight of said paste, or a mixture of 10% bis-GMA and 6.5% triethylene glycol dimethacrylate, both by weight of said paste.

The mixture is done in a ratio varying between 20 to 1 of paste to powder to 10 to 1 of paste to powder.

35 More specifically, this system may comprise the following, with resin, filler, etc., ingredients always lying within the above-given ranges and percentages being by weight:

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Paste:

<u>Ingredients</u>	<u>Percent by Weight</u>	
Bis-GMA	0	to 32
5 Ethoxylated bisphenol-A- dimethacrylate	0	to 63.4 (more specifically 16-63.4%)
Ethylene glycol dimethacrylate	0	to 24
Diethylene glycol dimethacrylate	0	to 24
10 Triethylene glycol dimethacrylate	0	to 24
Polyethylene glycol dimethacrylate	0	to 24
Barium glass	0	to 25
Lithium aluminum silicate	0	to 85
15 Flint silica		to 8.5
Borosilicate glass	0	to 85
Fumed synthetic silica	0	to 52
Strontium glass	0	to 85
20 Quartz	0	to 85
Titanium dioxide	0	to 0.13
Tinting agents (e.g., iron oxides)	0	to 4
A-174 Silane	0.05	to 1.25
25 Exciplex-forming photoinitiators	0.7	to 3.70
Glacial acetic acid	0.004	to 0.02

Powder:

<u>Ingredients</u>	<u>Percent by Weight</u>	
Barium glass	0	to 30
Lithium aluminum silicate	0	to 99.65
35 Flint silica	0	to 10
Borosilicate glass	0	to 99.65
Fumed synthetic silica	0	to 99.65
Strontium glass	0	to 99.65
40 Titanium dioxide	0	to 0.15
Tinting agent (e.g., iron oxides)	0	to 5
A-174 silane	0	to 6.0 (more sepcifically 1.25-5.25%)
Peroxide curing agent		
45 (e.g. benzoyl peroxide)	0.30	to 10
Glacial acetic acid	0.02	to 0.17

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EXAMPLE 14

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Paste-Powder SystemPaste:

	<u>Ingredients</u>	<u>Percentage by Weight</u>
5	Ethoxylated bisphenol-A-	
	dimethacrylate	63.40%
10	2,3-Bornanedione	0.056%
	Ethyl-4-dimethylamino	
	benzoate	3.1%
15	Fumed silica	16.05%
	Barium glass	16.59%
	Titanium dioxide	00.05%
	Yellow iron oxide	00.16%
20	Butylated hydroxytoluene	0.005%
	Glacial acetic acid	0.004%
	2-Hydroxy-4-methoxy	
25	benzophenone	0.585%

Powder:

	<u>Ingredients</u>	<u>Percentage by Weight</u>
30	Fumed silica	86.07%
	Benzoyl peroxide	8.60%
	A-174 silane	5.16%
35	Acetic acid	0.17%

When a small amount (10% by weight) of the powder is added to the paste, the resulting heavy paste has a working time of over 20 minutes. When so mixed and exposed to the Visar curing light for 30 seconds, the depth of cure measured at least 4.50 mm. Diametral tensile strength was 344.74×10^5 Pa (5000 psi).

EXAMPLE 15

Paste-Powder SystemPaste:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Bis-GMA	9.74%
Triethylene glycol	
dimethacrylate	6.49%
2,3-Bornanediol	0.03%
Ethyl-4-dimethylamino-	
benzoate	0.76%
Barium glass	24.52%
Lithium aluminum silicate	57.21%
A-174 silane	1.23%
Glacial acetic acid	0.02%

Powder:

<u>Ingredients</u>	<u>Percentage by Weight</u>
Barium glass	29.05%
Lithium aluminum silicate	67.78%
A-174 silane	1.45%
Benzoyl peroxide	1.696%
Glacial acetic acid	0.024%

The paste and powder are mixed at a weight ratio of 100:5, paste:powder. When so mixed and exposed to a Visar curing unit for 30 seconds, the depth of cure was 5.40 mm. The time to obtain a 12 mm cure was 25 minutes. The diametral tensile strength was $488.84 \times 10^5 \text{ Pa}$ (7090 psi).

EXAMPLE 16

Paste-Powder System

5	<u>Paste:</u>		
	<u>Ingredients</u>	<u>Percentage by Weight</u>	
	Ethoxylated bisphenol-A- dimethacrylate	12.98%	
10	Triethylene glycol dimethacrylate	3.25%	
	2,3-Bornanedione	0.03%	
15	Ethyl-4-dimethylamino- benzoate	0.76%	
	Barium glass	24.52%	
	Lithium aluminum silicate	57.21%	
20	A-174 silane	1.23%	
	Glacial acetic acid	0.02%	
25	<u>Powder:</u>		
	<u>Ingredients</u>	<u>Percentage by Weight</u>	
	Barium glass	29.05%	
30	Lithium aluminum silicate	67.78%	
	A-174 silane	1.45%	
	Benzoyl peroxide	1.696%	
35	Glacial acetic acid	0.024%	

The paste and powder are mixed together at a weight ratio of 100:5, paste:powder. When so mixed and exposed to the output from a Visar curing unit for 30 seconds, the depth of cure was 5.15 mm. The time to a 12 mm cure was 35 minutes. The diametral tensile strength was 362.10^5 Pa (5250 psi).

Gel-Powder Systems (c)

Using powder like that used in the powder-liquid system but employing a gel instead of a liquid, a general formulation for these systems may be as follows:

Gel:IngredientsPercentage by Weight

Resin	49	to 80.4
5 Filler	49	to 10.3
A-174 silane	0	to 1.25

10 photoinitiator 2 to 8

Glacial acetic acid 0 to 0.05

consisting essentially of about $\frac{3}{4}$ resin and $\frac{1}{4}$ filler

Powder:IngredientsPercentage by Weight

15 Filler	99.95	to 93.786
A-174 silane	0	to 1.50
20 Peroxide	0.05	to 4.69
Glacial acetic acid	0	to 0.024

The photoinitiator is made up of

25 (a) 2,3-bornanedione in an amount of 0.005 to 0.15% by weight of said gel and

(b) either ethyl-4-dimethyl-amino-benzoate or ethyl-2-dimethyl-amino-benzoate in an amount of 2.0 to 8%, more specifically 2.0 to 7.5%, by weight of said gel.

The mixture may vary from one part of powder to twenty parts of gel to three parts of powder to one part of gel.

30 More specifically, while adhering to the general formulation above, the system may use individual ingredients as follows:

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Gel:IngredientsPercent by Weight

	Bis-GMA	0	to 72
5	Ethoxylated bisphenol-A-dimethacrylate	0	to 90
	Ethylene glycol dimethacrylate	0	to 54
	Diethylene glycol dimethacrylate	0	to 54
	Triethylene glycol dimethacrylate	0	to 54
10	Polyethylene glycol dimethacrylate	0	to 54
	Barium glass	0	to 15
	Lithium aluminum silicate	0	to 50
	Flint silica		to 5.
15	Borosilicate glass	0	to 50
	Fumed synthetic silica	0	to 50
	Strontium glass	0	to 50
	Quartz	0	to 50
20	Titanium dioxide	0	to 1
	Tinting agents (e.g., iron oxides)	0	to 5
	A-174 Silane	0	to 1.25
	Exciplex-forming photoinitiators	2	to 8
25	Glacial acetic acid	0	to 0.05(more specifically 0.01-0.05%)

Powder:IngredientsPercent by Weight

30	Barium glass	0	to 30
	Lithium aluminum silicate	0	to 99.95
	Flint silica	0	to 10
35	Borosilicate glass	0	to 99.95
	Fumed synthetic silica	0	to 99.95
	Strontium glass	0	to 99.95
	Titanium dioxide	0	to 1.50
40	Tinting agent (e.g., iron oxides)	0	to 5
	A-174 silane	0	to 1.50(more specifically 0.05-1.50%)
	Peroxide curing agent (e.g. benzoyl peroxide)	0.05	to 4.69
45	Glacial acetic acid	0	to 0.024

More specifically, the filler for the gel component comprises, by weight of the gel, 2-5% barium glass, 5-10% lithium aluminium silicate and 7-10% fumed silica.

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EXAMPLE 17

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Gel-Powder SystemGel:

5	<u>Ingredients</u>	<u>Percentage by Weight</u>
10	Ethoxylated bisphenol-A- dimethacrylate	76.40%
	2,3-Bornanediene	0.06%
	Ethyl-4-dimethylamino benzoate	2.28%
15	Fumed silica	8.30%
	Barium glass	3.831%
	Lithium aluminum silicate	8.938%
20	A-174 silane	0.188%
	Glacial acetic acid	0.003%

25 Powder:

30 The powder is the same as that of Example 16. The powder and gel are mixed together in a weight ratio of 3:1, powder to gel. When exposed to a visible light dental curing unit for 30 seconds, the material cured to a depth of 4.90 mm. Under normal room fluorescent lighting, the paste had a workable time of approximately 35 minutes. The diametral tensile strength was $399.9 \cdot 10^5$ Pa (5800 psi).

EXAMPLE 18

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Gel-Powder System40 Gel:

	<u>Ingredients</u>	<u>Percentage by Weight</u>
45	Ethoxylated bisphenol-A- dimethacrylate	76.34%
	2,3-Bornanediene	0.14%
	Ethyl-4-dimethylamino benzoate	2.28%
50	Fumed silica	21.24%

55 Powder:

The powder is the same as that used in example 16. The powder and gel are mixed in a ratio of 3:1, powder to gel. When, exposed to a visible light dental curing unit 30 seconds, the material cured to a depth of 5.40 mm. Under normal fluorescent lighting, the paste has a workable time of 25 minutes. The diametral

tensile strength was $488.84 \cdot 10^5$ Pa (7090 psi).

This restorative system may be used in the repair of fractured porcelain material, natural teeth, or in any other intra-oral situation where a resin material is desired to replace or simulate tooth structure that is capable of being polymerized by visible light and having the process continue after the light is removed.

- 5 Also, this restorative system, which is essentially a light-cured system, achieves uniform polymerization within thirty minutes to one hour after insertion in the patient's mouth, even though variable amounts of light be radiated to the polymerizing resin.

This system eliminates the color changes that tend to occur when certain resins mixed with curing resins are exposed to ultra-violet or visible light.

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Claims

- 15 1. A two-part system for making a filled methacrylate-functional resin composition by mixture of the two parts, comprising:
 first part: dental-type methacrylate-functional resin with photoinitiator therefor;
 second part: dental-type filler powder with an accelerator-free peroxide curing agent for said resin;
 said photoinitiator being an exciplex of (1) either 2,3-bornanedione or benzil and (2)
 either ethyl 4-dimethylaminobenzoate or ethyl 2-dimethyl-aminobenzoate;
 said two-part system being any of
 (a) a paste-paste system,
 (b) a paste-powder system,
 (c) a gel-powder system,
 (d) a liquid-powder system, said photoinitiator, peroxide curing agent and first and second parts in
 said systems being present in an amount of:

system	photoinitiator		peroxide curing agent		part 1 : part 2
35 (a)	1.50-3.50	wt%	0.10-0.75	wt%	1 : 1
(b)	0.70-3.70	wt%	0.30-10.00	wt%	20:1 - 10:1
40 (c)	2.00-8.00	wt%	0.05-4.69	wt%	20:1 - 1:3
(d)	0.70-18.00	wt%	0.05-0.70	wt%	1:1 - 1:4

45 whereby the percentages are based on the components of that part of the system containing the respective compound.

2. The composition of claim 1 wherein said photoinitiator is 2,3-bornanedione with ethyl-4-dimethyl-amino-benzoate.
- 50 3. The composition of claim 1 wherein said photoinitiator is 2,3-bornanedione with ethyl-2-dimethyl-amino-benzoate.
4. The composition of claim 1 wherein said photoinitiator is benzil with ethyl-4-dimethyl-amino-benzoate.
- 55 5. The composition of claim 1 wherein said photoinitiator is benzil with ethyl-2-dimethyl-amino-benzoate.
6. The gel-powder system of any of claims 1-5 wherein the gel contains some filler.

7. the paste-paste system of any of claims 1-5 wherein both parts contain substantial amounts of filler.
8. A liquid-powder system according to claim 1 the powder component consisting essentially by weight of:

5	Dental filler-colorant material	99.85% to 97.7%
	Gamma-methacryloxy propyl	
	trimethoxy silane	0.10% to 1.55%
10	Peroxide curing agent	0.05% to 0.70%
	Glacial acetic acid	0 to 0.05%

and the liquid component consisting essentially, by weight of:

15	a methacrylate-functional resin	
	suitable for use in dental	
	composites	99.3% to 82%
20	exciplex-forming photoinitiator	
	for said resin	0.7% to 18%

- 25 9. The liquid-powder system according to claim 8 wherein:
said filler-colorant consists essentially by weight of ingredients totaling as in claim 8 and selected from:

30	Barium glass	0% to 30%
	Lithium aluminum silicate	0% to 99.85%
	Flint silica	0% to 10%
35	Borosilicate glass	0% to 99.85%
	Fumed synthetic silica	0% to 99.85%
	Quartz	0% to 99.85%
40	Custer feldspar	0% to 10%

said powder component also. including, in addition to the silane, the peroxide curing agent, and the glacial acetic acid:

45	Titanium dioxide	0% to 0.15%
	Metal salts	0% to 5.00%

50 said methacrylate-functional resin totaling as in claim 8 and consisting essentially by weight of ingredients:

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	Bis-GMA	0%	to 80%
	Ethoxylated bisphenol-A-		
5	dimethacrylate	0%	to 99%
	Ethylene glycol dimethacrylate	0%	to 60%
	Diethylene glycol dimethacrylate	0%	to 60%
	Triethylene glycol dimethacrylate	0%	to 60%
10	Polyethylene glycol dimethacrylate	0%	to 60%
	Exciplex forming photoinitiator	0.7%	to 18%

- 15 10. A liquid-powder system according to claim 1 wherein
- (a) the powder component consists essentially of a powdered dental filler-colorant, with a powdered peroxide curing agent in an amount between 0.05% and 0.7% by weight of said powder component, and
- 20 (b) the liquid component, consists essentially of
- (1) a methacrylate-functional resin suitable for use in dental composites in an amount of 84-96% by weight of said liquid component, and
- (2) a photoinitiator for said resin consisting of an exciplex incorporating as one ingredient either ethyl-4-dimethyl-amino-benzoate or ethyl-2-dimethyl-amino-benzoate in an amount of 0.7 to 10% by weight of said liquid component, the other ingredient being either 2,3-bornanedione or benzil and present in an amount of 0.01 - 8%, by weight of said liquid component, for a total photoinitiator amount by weight of said liquid component of 0.7 to 18% said powder and liquid components suitable to be mixed together just before use in a weight ratio of from 2:1 to 3.5:1 powder to liquid.

- 30 11. The system of claim 10, wherein said powder component, by weight of said powder component contains:

	Barium glass	23 - 30%
35	Lithium aluminum silicate	54 - 70%
	Flint silica	1 - 10%

- 40 for a total filler content of about 97.5 to 99.85%.

- 45 12. The system of claim 10 or 11 wherein said powder component also contains glacial acetic acid and gamma-methacryloxy propyl trimethoxy silane.
13. The system of claim 12 wherein said glacial acetic acid is present in an amount of 0.001 - 0.05%, by weight of said powder component, and said silane is present in an amount of 0.1% to 1.5% by weight of said powder component.
- 50 14. The system according to one or more of claims 10-13 wherein said resin is ethoxylated bisphenol-A-dimethacrylate in an amount of 82 to 99.3% by weight of said liquid component.
- 55 15. The system according to one or more of claims 10-13 wherein said resin is a mixture, by weight of said liquid component, of 60-84% ethoxylated bisphenol-A-dimethacrylate and 40-16% triethylene glycol dimethacrylate.

16. The system according to one or more of claims 10-13 wherein said resin is a mixture, by weight of said liquid component, of 55% Bis-GMA and 36% of triethylene glycol dimethacrylate.
17. The system according to one or more of claims 10-16 employing 2,3-bornanedione in amounts by weight of said liquid component of 0.02 - 0.2%.
18. The system according to one or more of claims 10-17 wherein said liquid component also includes BHT (butylated hydroxy toluene) in an amount of 0.02% by weight of said liquid component.
19. A two-paste system according to claim 1 for porcelain and dental restoration, said pastes suitable to be mixed together at the time of use in substantially equal amounts by weight,
both pastes containing methacrylate-functional resin suitable for use in dental components and dental filler material in an amount totaling over 95% thereof by weight of each paste.
20. The system of claim 19 in which each paste also contains gamma-methacryloxy propyl trimethoxy silane in an amount of 0.06 to 1.2% by weight of each paste.
21. The system of claim 20 in which at least one of the pastes also contains glacial acetic acid in an amount of at least 0.0015% by weight of that paste.
22. The system of one or more of claims 19-21 wherein said resin is ethoxylated bisphenol-A-dimethacrylate.
23. The system of one or more of claims 19-22 wherein said resin is present in the peroxide-containing paste in an amount of 14 - 40% and is present in the exciplex-containing paste in an amount of 14-36%.
24. The system of one or more of claims 19-23 where in said filler is chosen from (a) strontium glass and a mixture of barium glass with lithium aluminum silicate, and also includes fumed silica.
25. The system of claims 24 wherein the filler comprises, by weight of each paste about 1% of fumed silica and about 80% of strontium glass.
26. The system of claim 24 wherein the filler comprises, by weight of each paste, about 1% of fumed silica, 24% of barium glass, and 56-57% of lithium aluminum silicate.
27. A paste-powder system according to claim 1 for use in and porcelain restoration, the paste and powder suitable to be mixed at the time of use at a ratio of paste to powder of 10:1 to 20:1,
said paste comprising the mixture of methacrylate functional dental resin and powdered dental filler in a total amount lying between 96-98% by weight of the paste and having an exciplex, visual-light reactive photoinitiator,
said powder consisting essentially of a dental filler and a peroxide curing agent for the resin in an amount of 0.3% -10% of the powder,
said exciplex being made up of
(a) 2,3-bornanedione in an amount of about 0.03% to 0.06% by weight of said paste and,
(b) either ethyl-4-dimethyl-amino-benzoate or ethyl-2-dimethyl-amino-benzoate in an amount of about 0.75 to 3.25% by weight of said paste.
28. The system of any of claims 1,10 and 27 wherein said resin is selected from ethoxylated bisphenol-A-dimethacrylate, bis-GMA a mixture thereof with an ethylene glycol dimethacrylate, and a mixture of bis-GMA with an ethylene glycol dimethacrylate.
29. The system of claim 27 wherein the resin is from 16-63.4% ethoxylated bisphenol-A-dimethacrylate, by weight of said paste.
30. The system of claim 27 wherein the resin is a mixture of 13% ethoxylated bisphenol-A-dimethacrylate and 3.25% of triethylene glycol dimethacrylate, both by weight of said paste

31. The system of claim 27 where in the resin is a mixture of 10% bis-GMA and 6.5% triethylene glycol dimethacrylate, both by weight of said paste
32. The system of claims 27 wherein at least the powder contains gamma-methacryloxy propyl trimethoxy silane, in an amount of 1.25 to 5.25% by weight of its component.
33. The system of claim 27 or 32 wherein at least the powder contains glacial acetic acid in an amount of 0.02 to 0.17% by weight of its component.
34. A gel-powder system according to claim 1 for use in dental and porcelain restoration, the gel and powder suitable to be mixed at the time of use for cure by visible light, in a ratio of 20:1 to 1:3 of gel to powder,
the gel consisting essentially of about 3/4 methacrylate-functional dental resin and about 1/4 dental filler to a total amount of 90.7-98% by weight of said gel and an exciplex, visible-light-reactive photoinitiator having two ingredients (a) and (b),
said powder consisting essentially of a dental filler and an accelerator-free peroxide curing agent for said resin in an amount of 0.05%-4.69 % by weight of said powder,
said photoinitiator being made up of
(a) 2,3-bornanedione in an amount of 0.005 to 0.15% by weight of said gel and,
(b) either ethyl-4-dimethyl-amino-benzoate or ethyl-2-dimethyl-amino-benzoate in an amount of about 2.0 to 8% by weight of said gel.
35. The system of claim 34 wherein said resin is ethoxylated bisphenol-A-dimethacrylate.
36. The system of claim 10 or claims 34 wherein said filler for the powder component is selected from barium glass, strontium glass, lithium aluminum silicate, flint silica and mixtures of the members of this group with each others.
37. The system of claim 34 wherein said filler for the powder component is a mixture of barium glass, lithium aluminum silicate and flint silica.
38. The system of claim 37 wherein said filler for the powder component contains, by weight of the powder, 23-30% barium glass, 54-70% lithium aluminum silicate and 1-10% flint silica.
39. The system of claim 27 or claim 34 wherein said filler for the gel component is fumed silica.
40. The system of claim 27 or claim 34 wherein said filler for the gel component comprises a mixture of barium glass and lithium aluminum silicate.
41. The system of claim 34 wherein said filler for the gel component comprises, by weight of the gel, 2-5% barium glass, 5-10% lithium aluminum silicate and 7-10% fumed silica.
42. The system of claim 34 wherein at least the powder component contains gamma-methacryloxy propyl trimethoxy silane, in an amount of 0.05 to 1.5% by weight of its component.
43. The system of claim 34 wherein at least the gel component contains glacial acetic acid, in an amount of 0.01 to 0.05% by weight of its component.
44. A method for repairing porcelain or teeth with the aid of a two-part system, said method comprising the steps of:
mixing together under ordinary indoor lighting conditions:
- a methacrylate functional resin usable in dental composites and photoinitiator for said resin, said photoinitiator being an exciplex of (1) either 2,3-bornanedione or benzil and (2) either ethyl 4-dimethylaminobenzoate or ethyl 2-dimethylaminobenzoate (part 1), and
- powdered dental filler-colorant and at least one accelerator-free peroxide curing agent for said resin (part 2), said two-part system being either
(a) a paste-paste system
(b) a paste-powder system.

(c) a gel-powder system or
 (d) a liquid-powder system, said photoinitiator, peroxide curing agent and first and second parts in said systems being present in an amount of:

system	photoinitiator		peroxide curing agent		part 1 : part 2
(a)	1.50-3.50	wt%	0.10-0.75	wt%	1 : 1
(b)	0.70-3.70	wt%	0.30-10.00	wt%	20:1 - 10:1
(c)	2.00-8.00	wt%	0.05-4.69	wt%	20:1 - 1:3
(d)	0.70-18.00	wt%	0.05-0.70	wt%	1:1 - 1:4

whereby the percentages are based on the components of that part of the system containing the respective compound;

emplacing the mixture within a few minutes of the mixing, and curing a substantial portion of the emplaced mixture in situ for one half-minute under intense visual-light illumination of at least 53800 lx (5,000 foot candles), any resin then uncured by light being cured within the next hour by said peroxide curing agent, with the exception of those methods falling under the scope of Art. 52(4) EPC.

45. The method of claims 44 wherein the resin is at least one resin chosen from ethoxylated bisphenol-A-dimethacrylate, bis-GMA, and an adduct of 2,2'-propane bis [3-(4-phenoxy)-1,2-dihydroxy propane-1 methacrylate] and mono- or di- isocyanate.

46. The method of claim 44 using a liquid-powder system and wherein said exciplex constitutes 0.7% to 18% by weight of said liquid mixture and said peroxide constitutes about 0.05 to about 0.7% of said powder mixture.

47. The method of claim 44 using a liquid-powder system and having the step in between preparing and mixing of storing said powder in a container and of storing said liquid in an opaque container.

48. The method of claim 44 using a paste-paste system wherein said first paste, at least, is prepared long in advance and comprising the step of storing said first paste in an opaque container until said mixing step.

49. The method of claim 44 using a paste-paste system in which said exciplex constitutes 1.5 to 3.5% by weight of said first paste and said peroxide constitutes 0.1 to 0.75% by weight of said second paste.

50. The method of claim 44 using a paste-powder system wherein said mixing of said paste is done well in advance of use including the step of storing said paste in an opaque container prior to said mixing of the powder with the paste.

51. The method of claim 44 using a paste-powder system wherein said exciplex constitutes 0.7 to 3.7% of said paste and said peroxide constitutes 0.3 to 10% of said powder.

52. A method according to claim 44 using a gel-powder system, said method comprising:

mixing together under ordinary indoor lighting conditions,

a gel consisting essentially of about 3/4 methacrylate-functional dental resin and about 1/4 dental filler to a total amount of 90.7 to 98% by weight of the gel and an exciplex; visible-light-reactive photoinitiator having two ingredients, one of which is

(a) 2,3-bormanedione in an amount of 0.005 to 0.15% by weight and the other is

(b) ethyl-4-dimethyl-amino-benzoate or ethyl-2-dimethyl-amino-benzoate, in an amount of 2% to

8% by weight of the gel,
with a powder consisting essentially of a filler and an accelerator free peroxide curing agent for the resin in an amount of 0.05%-4.69% by weight of the powder,
in a ratio of 20:1 to 1:3 of gel to powder.

53. The method of claim 51 wherein the resin is ethoxylated bisphenol-A-dimethacrylate.
54. The method of claim 52 wherein the filler for the gel component is fumed silica.
55. The method of claim 52 wherein the filler for the gel component comprises, by weight of the gel, 2-5%-barium glass, 5-10% lithium aluminum silicate and 7-10% fumed silica.
56. The method of claim 52 wherein the exciplex is made up of
(a) either 2,3-bornanedione or benzil in an amount of 0.005 to 0.15% by weight of the gel and,
(b) either ethyl-4-dimethyl-amino-benzoate or ethyl-2-dimethyl-amino-benzoate in an amount of 2.0 to 7.5% by weight of the gel.
57. The method of claim 52 wherein the filler for the powder component is selected from barium glass, lithium aluminum silicate, flint silica and mixtures of the members of this group with each other.
58. The method of claims 52 wherein the filler for the powder component contains, by weight of the powder, 23-30% barium glass, 54-70% lithium aluminum silicate and 1-10% flint silica.
59. A method for preparing a two-part storable filled-resin composition useful for porcelain repair and as a dental composite comprising:
coating, in order to prepare the second part, a powdered dental filler with at least one accelerator-free peroxide curing agent for said resin,
storing said filler;
mixing, in order to prepare the first part, an uncured methacrylate functional resin usable in dental composites with photoinitiator for said resin,
said photoinitiator being an exciplex of (1) either 2,3-bornanedione or benzil and (2) either ethyl 4-dimethylaminobenzoate or ethyl 2-dimethylaminobenzoate,
storing the resin-photoinitiator mixture in an opaque container;
said two-part system being either
(a) a paste-paste system,
(b) a paste-powder system,
(c) a gel-powder system or
(d) a liquid-powder system,
said photoinitiator, peroxide curing agent and first and second parts in said systems being present in an amount of:

system	photoinitiator		peroxide curing agent		part 1 : part 2
(a)	1.50-3.50	wt%	0.10-0.75	wt%	1 : 1
(b)	0.70-3.70	wt%	0.30-10.00	wt%	20:1 - 10:1
(c)	2.00-8.00	wt%	0.05-4.69	wt%	20:1 - 1:3
(d)	0.70-18.00	wt%	0.05-0.70	wt%	1:1 - 1:4

whereby the percentages are based on the components of that part of the system containing the

respective compound.

60. A system or method according to any of the preceding claims wherein the peroxide curing agent is benzoyl peroxide.

5

Revendications

1. Système à deux composants, pour produire une composition de résine chargée à fonction méthacrylate, par mélange des deux composants, comprenant :
- premier composant : une résine de type dentaire à fonction méthacrylate, avec un photo-amorceur pour elle ;
- second composant : poudre de charge de type dentaire, avec un durcisseur peroxyde exempt d'accélérateur pour ladite résine ; ledit photo-amorceur étant un exciplexe de (1) la 2,3-bornanedione ou le benzile et (2) le 4-diméthylamino-benzoate d'éthyle ou le 2-diméthylamino-benzoate d'éthyle ;
- ledit système à deux composants étant l'un quelconque de
- (a) un système pâte-pâte,
- (b) un système pâte-poudre,
- (c) un système gel-poudre,
- (d) un système liquide-poudre, lesdits photo-amorceur, durcisseur peroxyde, et premier et second composants dans lesdits systèmes étant présents en les proportions suivantes :

Système	photo-amorceur	durcisseur peroxyde	composant 1 : composant 2
(a)	1,50 - 3,50 % pds	0,10 - 0,75 % pds	1 : 1
(b)	0,70 - 3,70 % pds	0,30 - 10,00 % pds	20:1 - 10:1
(c)	2,00 - 8,00 % pds	0,05 - 4,69 % pds	20:1 - 1:3
(d)	0,70 - 18,00 % pds	0,05 - 0,70 % pds	1:1 - 1:4

cès pourcentages étant rapportés au total des éléments du composant du système contenant le composé considéré.

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2. Composition selon la revendication 1, dans laquelle ledit photo-amorceur est la 2,3-bornanedione associée au 4-diméthylamino-benzoate d'éthyle.
3. Composition selon la revendication 1, dans laquelle ledit photo-amorceur est la 2,3-bornanedione associée au 2-diméthylamino-benzoate d'éthyle.
4. Composition selon la revendication 1, dans laquelle ledit photo-amorceur est le benzile associé au 4-diméthylamino-benzoate d'éthyle.
5. Composition selon la revendication 1, dans laquelle ledit photo-amorceur est le benzile associé au 2-diméthylamino-benzoate d'éthyle.
6. Système gel-poudre selon l'une quelconque des revendications 1-5, dans lequel le gel contient une certaine quantité de charge.
7. Système pâte-pâte selon l'une quelconque des revendications 1-5, dans lequel les deux composants contiennent des proportions importantes de charge.
8. Système liquide-poudre selon la revendication 1, le composant poudre comprenant essentiellement (en poids) :
- 99,85 % à 97,7 % de charge colorante dentaire,
- 0,10 % à 1,55 % de gamma-méthacryloxypropyl-triméthoxysilane,
- 0,05 % à 0,70 % d'agent durcisseur peroxyde,

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0 à 0,05 % d'acide acétique glacial, et le composant liquide comprenant essentiellement (en poids) :
 99,3 % à 82 % d'une résine à fonction méthacrylate, convenant à l'emploi dans des composites dentaires,
 0,7 % à 18 % d'un photo-amorceur formant un exciplexe pour ladite résine.

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9. Système poudre-liquide selon la revendication 8, dans lequel :

ladite charge colorante comprend essentiellement des ingrédients dont le total est tel qu'indiqué dans la revendication 8 et qui sont choisis parmi (pourcentages en poids) :

10	Verre au baryum	0 - 30 %
	Aluminosilicate de lithium	0 - 99,85 %
	Silice flint	0 - 10 %
15	Verre borosilicaté	0 - 99,85 %
	Silice synthétique fumée	0 - 99,85 %
	Quartz	0 - 99,85 %
20	Custérite (feldspath)	0 - 10 %

ledit composant poudre comprenant également, en plus du silane, du durcisseur peroxyde et de l'acide acétique glacial,

25	Dioxyde de titane	0 - 0,15 %
	Sels métalliques	0 - 5,00 %

ladite résine à fonction méthacrylate, dont la quantité totale est celle indiquée dans la revendication 8, comprenant essentiellement les ingrédients suivants (pourcentages en poids) :

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	Bis-GMA	0 - 80 %
	Diméthacrylate de bisphénol-A éthoxylé	0 - 99 %
35	Diméthacrylate d'éthylèneglycol	0 - 60 %
	Diméthacrylate de diéthylèneglycol	0 - 60 %
	Diméthacrylate de triéthylèneglycol	0 - 60 %
40	Diméthacrylate de polyéthylèneglycol	0 - 60 %
	Photo-amorceur formant des exciplexes	0,7 - 18 %

10. Système liquide-poudre selon la revendication 1, dans lequel

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(a) le composant poudre est constitué essentiellement d'une charge colorante dentaire pulvérulente, et d'un durcisseur peroxyde pulvérulent en une proportion située entre 0,05 % et 0,7 % en poids dudit composant poudre, et

(b) le composant liquide est essentiellement constitué de

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(1) une résine à fonction méthacrylate, appropriée pour être utilisée dans des composites dentaires, en une proportion de 84 - 96 % en poids dudit composant liquide, et

(2) un photo-amorceur pour ladite résine, constitué d'un exciplexe comprenant, comme l'un de ses ingrédients, le 4-diméthylamino-benzoate d'éthyle ou le 2-diméthylamino-benzoate d'éthyle en une proportion de 0,7 à 10 % en poids dudit composant liquide, l'autre ingrédient, qui est de la 2-3-bornanedione ou du benzile, étant présent en une proportion de 0,01 - 8 % en poids dudit composant liquide, la quantité totale du photo-amorceur étant de 0,7 à 18 % en poids dudit composant liquide, lesdits composants poudre et liquide étant adaptés pour être mélangés ensemble juste avant l'emploi, en un rapport pondéral de la poudre au liquide de 2:1 à 3,5:1.

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11. Système selon la revendication 10, dans lequel ledit composant poudre contient, en poids par rapport au poids dudit composant poudre :

5	Verre au baryum	23 - 30 %
	Aluminosilicate de lithium	54 - 70 %
	Silice flint	1 - 10 %
10	pour une teneur totale de charge d'environ 97,5 à 99,85 %.	

12. Système selon la revendication 10 ou 11, dans lequel ledit composant poudre contient également de l'acide acétique glacial et du gamma-méthacryloxypropyl-triméthoxysilane.

13. Système selon la revendication 12, dans lequel ledit acide acétique glacial est présent en une proportion de 0,001 - 0,05 % en poids dudit composant poudre, et ledit silane est présent en une proportion de 0,1 % à 1,5 % en poids dudit composant poudre.

14. Système conforme à l'une ou plusieurs des revendications 10 à 13, dans lequel ladite résine est du diméthacrylate de bisphénol-A éthoxylé, en une proportion de 82 à 99,3 % en poids dudit composant liquide.

15. Système conforme à l'une ou plusieurs des revendications 10 à 13, dans lequel ladite résine est un mélange, en poids et par rapport audit composant liquide, de 60 - 84 % de diméthacrylate de bisphénol-A éthoxylé et de 40 - 16 % de diméthacrylate de triéthylèneglycol.

16. Système conforme à l'une ou plusieurs des revendications 10 à 13, dans lequel ladite résine est un mélange, en poids et par rapport audit composant liquide, de 55 % de bis-GMA et de 36 % de diméthacrylate de triéthylèneglycol.

17. Système conforme à l'une ou plusieurs des revendications 10 à 16, et utilisant de la 2,3-bornanedione en des proportions pondérales de 0,02 à 0,2 % dudit composant liquide.

18. Système conforme à l'une ou plusieurs des revendications 10 à 17, dans lequel ledit composant liquide comprend également du BHT (hydroxytoluène butylé) en une proportion pondérale de 0,02 % dudit composant liquide.

19. Système à deux pâtes conforme à la revendication 1, pour la restauration de porcelaine et la restauration dentaire, lesdites pâtes étant appropriées pour être mélangées ensemble au moment de l'utilisation en des quantités pondérales à peu près égales,

les deux pâtes contenant une résine à fonction méthacrylate, appropriée pour être utilisée dans des composants dentaires, et un matériau de charge dentaire, en une quantité représentant au total plus de 95 % en poids de chaque pâte.

20. Système selon la revendication 19, dans lequel chaque pâte contient aussi du gamma-méthacryloxypropyl-triméthoxysilane, en une proportion pondérale de 0,06 à 1,2 % de chaque pâte.

21. Système selon la revendication 20, dans lequel au moins une des pâtes contient également de l'acide acétique glacial en une proportion pondérale d'au moins 0,0015 % de cette pâte.

22. Système selon l'une ou plusieurs des revendications 19 à 21, dans lequel ladite résine est du diméthacrylate de bisphénol-A éthoxylé.

23. Système selon l'une ou plusieurs des revendications 19 à 22, dans lequel ladite résine est présente, dans la pâte contenant le peroxyde, en une proportion de 14 à 40 %, et, dans la pâte contenant l'exciplexe, en une proportion de 14 à 36%.

24. Système selon l'une ou plusieurs des revendications 19 à 23, dans lequel ladite charge est choisie parmi (a) du verre au strontium et un mélange de verre au baryum avec de l'aluminosilicate de lithium, et comprend également de la silice fumée.
- 5 25. Système selon la revendication 24, dans lequel la charge comprend, par rapport au poids de chaque pâte, environ 1 % de silice fumée et environ 80 % de verre au strontium.
26. Système selon la revendication 24, dans lequel la charge comprend, par rapport au poids de chaque pâte, environ 1 % de silice fumée, 24 % de verre au baryum et 56 - 57 % d'aluminosilicate de lithium.
- 10 27. Système pâte-poudre conforme à la revendication 1, destiné à être utilisé dans la restauration dentaire et dans la réparation de porcelaine, la pâte et la poudre étant appropriées pour être mélangées au moment de l'utilisation, en un rapport pâte/poudre de 10/1 à 20/1,
ladite pâte comprenant le mélange de résine dentaire à fonction méthacrylate et de charge dentaire pulvérulente, en une quantité totale située entre 96 et 98 % en poids de la pâte et contenant un
15 photo-amorceur exciplexe, réagissant à la lumière visible,
ladite poudre étant constituée essentiellement d'une charge dentaire et d'un durcisseur peroxyde pour la résine en une proportion de 0,3 à 10 % de la poudre,
ledit exciplexe étant constitué de
20 (a) 2,3-bornanedione en une proportion pondérale d'environ 0,03 % à 0,06 % de ladite pâte, et
(b) 4-diméthylamino-benzoate d'éthyle ou 2-diméthylamino-benzoate d'éthyle, en une proportion pondérale d'environ 0,75 à 3,25 % de ladite pâte.
28. Système selon l'une quelconque des revendications 1, 10 et 27, dans lequel ladite résine est choisie
25 parmi le diméthacrylate de bisphénol-A éthoxylé, le bis-GMA, un mélange de ceux-ci avec du diméthacrylate d'éthylèneglycol, et un mélange de bis-GMA avec du diméthacrylate d'éthylèneglycol.
29. Système selon la revendication 27, dans lequel la résine est constituée de diméthacrylate de bisphénol-A éthoxylé, en une proportion pondérale de 16 à 63,4 % de ladite pâte.
- 30 30. Système selon la revendication 27, dans lequel la résine est un mélange de 13 % de diméthacrylate de bisphénol-A éthoxylé et de 3,25 % de diméthacrylate de triéthylèneglycol, dans les deux cas en proportion pondérale rapportée à ladite pâte.
- 35 31. Système selon la revendication 27, dans lequel la résine est un mélange de 10 % de bis-GMA et de 6,5 % de diméthacrylate de triéthylèneglycol, dans les deux cas en proportion pondérale rapportée à ladite pâte.
32. Système selon la revendication 27, dans lequel au moins la poudre contient du gamma-méthacryloxypropyl-triméthoxysilane, à raison de 1,25 à 5,25 % en poids de ce composant.
- 40 33. Système selon la revendication 27 ou 32, dans lequel au moins la poudre contient de l'acide acétique glacial à raison de 0,02 à 0,17 % en poids de ce composant.
- 45 34. Système gel-poudre conforme à la revendication 1, destiné à être utilisé dans la restauration dentaire et la réparation de porcelaine, le gel et la poudre étant appropriés pour être mélangés au moment de l'emploi, pour durcissement sous l'action d'une lumière visible, en un rapport gel/poudre de 20/1 à 1/3,
le gel étant constitué essentiellement d'environ 3/4 de résine dentaire à fonction méthacrylate et d'environ 1/4 de charge dentaire, pour une proportion pondérale totale de 90,7 à 98 % dudit gel, et
50 d'un photo-amorceur exciplexe, réagissant à une lumière visible, constitué de deux ingrédients (a) et (b),
ladite poudre étant constituée essentiellement d'une charge dentaire et d'un durcisseur peroxyde exempt d'accélérateur pour ladite résine, en une proportion pondérale de 0,05 % à 4,69 % de ladite poudre,
55 ledit photo-amorceur étant constitué par
(a) de la 2,3-bornanedione en une proportion pondérale de 0,005 à 0,15 % dudit gel, et
(b) du 4-diméthylamino-benzoate d'éthyle ou du 2-diméthylamino-benzoate d'éthyle, en une proportion pondérale d'environ 2,0 à 8 % dudit gel.

35. Système selon la revendication 34, dans lequel ladite résine est du diméthacrylate de bisphénol-A éthoxylé.
36. Système selon la revendication 10 ou la revendication 34, dans lequel ladite charge pour le composant poudre est choisie parmi du verre au baryum, du verre au strontium, de l'aluminosilicate de lithium, de la silice flint et des mélanges entre les éléments de ce groupe.
37. Système selon la revendication 34, dans lequel ladite charge pour le composant poudre est un mélange de verre au baryum, d'aluminosilicate de lithium et de silice flint.
38. Système selon la revendication 37, dans lequel ladite charge pour le composant poudre contient, par rapport au poids de la poudre, 23 - 30 % de verre au baryum, 54 - 70 % d'aluminosilicate de lithium et 1 - 10 % de silice flint.
39. Système selon la revendication 27 ou la revendication 34, dans lequel ladite charge pour le composant gel est de la silice fumée.
40. Système selon la revendication 27 ou la revendication 34, dans lequel ladite charge pour le composant gel comprend un mélange de verre au baryum et d'aluminosilicate de lithium.
41. Système selon la revendication 34, dans lequel ladite charge pour le composant gel comprend, par rapport au poids du gel, 2 - 5 % de verre au baryum, 5 - 10 % d'aluminosilicate de lithium et 7 - 10 % de silice fumée.
42. Système selon la revendication 34, dans lequel au moins le composant poudre contient du gamma-méthacryloxypropyl-triméthoxysilane, à raison de 0,05 à 1,5 % en poids de ce composant.
43. Système selon la revendication 34, dans lequel au moins le composant gel contient de l'acide acétique glacial, à raison de 0,01 à 0,05 % en poids de ce composant.
44. Procédé pour réparer de la porcelaine ou restaurer des dents à l'aide d'un système à deux composants, ledit procédé comprenant les étapes consistant à:
- mélanger ensemble, dans des conditions d'éclairage intérieur ordinaires,
 - une résine à fonction méthacrylate utilisable dans des composites dentaires et un photo-amorceur pour ladite résine, ledit photo-amorceur étant un exciplexe de (1) 2,3-bornanedione ou benzile et de (2) 4-diméthylamino-benzoate d'éthyle ou 2-diméthylamino-benzoate d'éthyle (composant 1), et
 - une charge colorante dentaire pulvérulente et au moins un durcisseur peroxyde exempt d'accélérateur pour ladite résine (composant 2), ledit système à deux composants étant
 - (a) un système pâte-pâte,
 - (b) un système pâte-poudre,
 - (c) un système gel-poudre, ou
 - (d) un système liquide-poudre, lesdits photo-amorceur, durcisseur peroxyde, et premier et second composants dans lesdits systèmes étant présents en les proportions suivantes :

Système	photo-amorceur	durcisseur peroxyde	composant 1 / composant 2
(a)	1,50 - 3,50 % pds	0,10 - 0,75 % pds	1 / 1
(b)	0,70 - 3 70 % pds	0,30 - 10,00 % pds	20/1 - 10/1
(c)	2,00 - 8,00 % pds	0,05 - 4,69 % pds	20/1 - 1/3
(d)	0,70 - 18,00 % pds	0,05 - 0,70 % pds	1/1 - 1/4

les pourcentages étant rapportés aux constituants du composant du système contenant le composé considéré ; mettre le mélange en place en quelques minutes après le mélange, et faire durcir une partie importante du mélange mis en place in situ pendant une demi-minute sous éclairage

intense par de la lumière visible, d'au moins 53 800 lux (5000 pieds-candelas), toute résine n'ayant pas alors durci sous l'action de la lumière durcissant dans l'heure suivante grâce audit durcisseur peroxyde,
à l'exception des procédés tombant dans le cadre de l'article 52(4) de la CBE.

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45. Procédé selon la revendication 44, dans lequel la résine est au moins une résine choisie parmi le diméthacrylate de bisphénol-A éthoxylé, le bis-GMA et un produit d'addition du 2,2'-propane-bis-[3-(4-phénoxy)-1,2-dihydroxypropane-1-méthacrylate] et d'un monoiso cyanate ou d'un diisocyanate.

10 46. Procédé selon la revendication 44, dans lequel on utilise un système liquide-poudre, ledit exciplexe constitue de 0,7 à 18 % en poids dudit mélange liquide, et ledit peroxyde constitue d'environ 0,05 à environ 0,7 % dudit mélange pulvérulent.

15 47. Procédé selon la revendication 44, dans lequel on utilise un système liquide-poudre et qui comprend l'étape consistant, entre la préparation et le mélange, à conserver ladite poudre dans un récipient et à conserver ledit liquide dans un récipient opaque.

20 48. Procédé selon la revendication 44, dans lequel on utilise un système pâte-pâte et ladite première pâte, au moins, est préparée longtemps à l'avance, et qui comprend l'étape consistant à conserver ladite première pâte dans un récipient opaque jusqu'à ladite étape de mélange.

49. Procédé selon la revendication 44, dans lequel on utilise un système pâte-pâte, ledit exciplexe constitue de 1,5 à 3,5 % en poids de ladite première pâte, et ledit peroxyde constitue de 0,1 à 0,75 % en poids de ladite seconde pâte.

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50. Procédé selon la revendication 44, dans lequel on utilise un système pâte-poudre et ledit mélange de ladite pâte est exécuté longtemps avant l'emploi, et qui comporte l'étape consistant à conserver ladite pâte dans un récipient opaque avant ledit mélange de la poudre avec la pâte.

30 51. Procédé selon la revendication 44, dans lequel on utilise un système pâte-poudre, ledit exciplexe représente de 0,7 à 3,7 % de ladite pâte, et ledit peroxyde représente de 0,3 à 10 % de ladite poudre.

52. Procédé conforme à la revendication 44, dans lequel on utilise un système gel-poudre, ledit procédé comprenant :

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le mélange, dans des conditions d'éclairage intérieur ordinaires,

d'un gel constitué essentiellement d'environ 3/4 de résine dentaire à fonction méthacrylate et d'environ 1/4 de charge dentaire, pour une quantité totale de 90,7 à 98 % en poids du gel, et d'un photo-amorceur exciplexe, réagissant à la lumière visible, comportant deux ingrédients dont l'un est (a) de la 2-3-bornanedione en une quantité de 0,005 à 0,15 % en poids et l'autre est (b) du 4-diméthylamino-benzoate d'éthyle ou du 2-diméthylamino-benzoate d'éthyle, en une quantité de 2 % à 8 % en poids du gel,

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avec une poudre constituée essentiellement d'une charge et d'un durcisseur peroxyde exempt d'accélérateur pour la résine, en une quantité de 0,05 à 4,69 % en poids de la poudre, en un rapport du gel à la poudre de 20:1 à 1:3.

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53. Procédé selon la revendication 52, dans lequel la résine est du diméthacrylate de bisphénol-A éthoxylé.

54. Procédé selon la revendication 52, dans lequel la charge pour le composant gel est de la silice fumée.

50 55. Procédé selon la revendication 52, dans lequel la charge pour le composant gel comprend, par rapport au poids du gel, de 2 à 5 % de verre au baryum, de 5 à 10 % d'aluminosilicate de lithium et de 7 à 10 % de silice fumée.

56. Procédé selon la revendication 52, dans lequel l'exciplexe est constitué de

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(a) 2,3-bornanedione ou benzile, à raison de 0,005 à 0,15 % en poids du gel, et de

(b) 4-diméthylamino-benzoate d'éthyle ou 2-diméthylamino-benzoate d'éthyle, à raison de 2,0 à 7,5 % en poids du gel.

57. Procédé selon la revendication 52, dans lequel la charge pour le composant poudre est choisie parmi le verre au baryum, l'aluminosilicate de lithium, la silice flint et des mélanges des éléments de ce groupe les uns aux autres.
58. Procédé selon la revendication 52, dans lequel la charge pour le composant poudre contient, par rapport au poids de la poudre, de 23 à 30 % de verre au baryum, de 54 à 70 % d'aluminosilicate de lithium et de 1 à 10 % de silice flint.
59. Procédé de préparation d'une composition de résine chargée en deux composants, pouvant être conservée, utilisable pour la réparation de porcelaine et comme composite dentaire, comprenant :
- le revêtement, afin de préparer le second composant, d'une charge dentaire pulvérulente avec au moins un durcisseur peroxyde exempt d'accélérateur pour ladite résine, la conservation de ladite charge,
 - le mélange, afin de préparer le premier composant, d'une résine non durcie à fonction méthacrylate, utilisable dans des composites dentaires, avec un photoamorceur pour ladite résine, ledit photo-amorceur étant un exciplexe de (1) 2,3-bornanedione ou benzile et de (2) 4-diméthylamino-benzoate d'éthyle ou 2-diméthylamino-benzoate d'éthyle, la conservation du mélange de résine et de photoamorceur dans un récipient opaque, ledit système à deux composants étant
 - (a) un système pâte-pâte,
 - (b) un système pâte-poudre,
 - (c) un système gel-poudre, ou
 - (d) un système liquide-poudre, lesdits photo-amorceur, durcisseur peroxyde et premier et second composants dans lesdits systèmes étant présents dans les proportions suivantes :

Système	photo-amorceur	durcisseur peroxyde	composant 1 / composant 2
(a)	1,50 - 3,50 % pds	0,10 - 0,75 % pds	1 / 1
(b)	0,70 - 3 70 % pds	0,30 - 10,00 % pds	20/1 - 10/1
(c)	2,00 - 8,00 % pds	0,05 - 4,69 % pds	20/1 - 1/3
(d)	0,70 - 18,00 % pds	0,05 - 0,70 % pds	1/1 - 1/4

les pourcentages étant rapportés aux constituants du composant du système contenant le composé considéré.

60. Système ou procédé conforme à l'une quelconque des revendications précédentes, dans lequel le durcisseur peroxyde est du peroxyde de benzoyle.

Ansprüche

1. Zweikomponentensystem zur Herstellung einer gefüllten methacrylatfunktionellen Harzmasse durch Mischen der beiden Komponenten, umfassend:
- erste Komponente: methacrylatfunktionelles Harz vom Dentaltyp mit Photoinitiator hierfür;
 - zweite Komponente: Füllstoffpulver vom Dentaltyp mit einem beschleunigerfreien Peroxidhärter für das Harz;
- wobei der Photoinitiator ein Exciplex von (1) entweder 2,3-Bornandion oder Benzil und (2) entweder Ethyl-4-dimethylaminobenzoat oder Ethyl-2-dimethylaminobenzoat ist;
- wobei das Zweikomponentensystem ein beliebiges System von
- (a) einem Pasten-Pasten-system,
 - (b) einem Pasten-Pulver-system,
 - (c) einem Gel-Pulver-system,
 - (d) einem Flüssigkeit-Pulver-system ist, wobei der Photoinitiator, der Peroxidhärter und die erste und

zweite Komponente in diesen Systemen in einer Menge vorliegen von:

System	Photoinitiator	Peroxid- härter	Kompo- nente 1	Kompo- nente 2
5	(a) 1,50-3,50 Gew.-%	0,10-0,75 Gew.-%	1 : 1	
	(b) 0,70-3,70 Gew.-%	0,30-10,00 Gew.-%	20:1 - 10:1	
10	(c) 2,00-8,00 Gew.-%	0,05-4,69 Gew.-%	20:1 - 1:3	
	(d) 0,70-18,00 Gew.-%	0,05-0,70 Gew.-%	1:1 - 1:4	

15 wobei die Prozentsätze auf die Bestandteile derjenigen Komponente des Systems bezogen sind, welche die jeweilige Verbindung enthalten.

2. Zusammensetzung nach Anspruch 1, in welcher der Photoinitiator 2,3-Bornandion mit Ethyl-4-dimethylaminobenzoat ist.
- 20 3. Zusammensetzung nach Anspruch 1, worin der Photoinitiator 2,3-Bornandion mit Ethyl-2-dimethylaminobenzoat ist.
4. Zusammensetzung nach Anspruch 1, worin der Photoinitiator Benzil mit Ethyl-4-dimethylaminobenzoat ist.
- 25 5. Zusammensetzung nach Anspruch 1, worin der Photoinitiator Benzil mit Ethyl-2-dimethylaminobenzoat ist.
6. Gel-Pulver-system nach einem der Ansprüche 1-5, worin das Gel etwas Füllstoff enthält.
- 30 7. Pasten-Pasten-system nach einem der Ansprüche 1-5, worin beide Komponenten wesentliche Mengen an Füllstoff enthalten.
8. Flüssigkeits-Pulver-system nach Anspruch 1, wobei der Pulverbestandteil im wesentlichen in Gewicht besteht aus:
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40	Dentalfüllstoff-Farbgebungs- material	99,85% bis 97,7%
	gamma-Methacryloxypropyl- trimethoxysilan	0,10% bis 1,55%
	Peroxidhärter	0,05% bis 0,70%
45	Eisessig	0 bis 0,05%

und die Flüssigkomponente im wesentlichen in Gewicht besteht aus:

50	einem methacrylat-funktionellen Harz, das zur Verwendung in Dentalverbundstoffen geeignet ist	99,3% bis 82%
55	Exciplex-bildendem Photoinitiator für dieses Harz	0,7% bis 18%.

9. Flüssigkeits-Pulver-system nach Anspruch 8, worin:
der Füllstoff-Farbgeber im wesentlichen in Gewicht aus Inhaltsstoffen in der Gesamtmenge wie in
Anspruch 8 besteht und ausgewählt ist aus:

5	Bariumglas	0% bis 30%
	Lithiumaluminiumsilikat	0% bis 99,85%
	Flintkieselerde	0% bis 10%
10	Borsilikatglas	0% bis 99,85%
	synthetische, pyrogene Kieselsäure	0% bis 99,85%
	Quarz	0% bis 99,85%
15	Custer-Feldspat	0% bis 10%,

wobei der Pulverbestandteil zusätzlich zu dem Silan, dem Peroxidhärter und dem Eisessig noch
einschließt:

20	Titandioxid	0% bis 0,15%
	Metallsalze	0% bis 5,00%

- 25 wobei das methacrylat-funktionelle Harz der Gesamtmenge wie in Anspruch 8 entspricht und im
wesentlichen in Gewicht besteht aus den Bestandteilen:

	Bis-GMA	0% bis 80%
30	ethoxyliertem Bisphenol-A- dimethacrylat	0% bis 99%
	Ethylenglycoldimethacrylat	0% bis 60%
35	Diethylenglycoldimethacrylat	0% bis 60%
	Triethylenglycoldimethacrylat	0% bis 60%
	Polyethylenglycoldimethacrylat	0% bis 60%
40	Exciplex-bildendem Photoinitiator	0,7% bis 18%

10. Flüssigkeits-Pulver-system nach Anspruch 1, worin:

- 45 (a) der pulverbestandteil im wesentlichen aus einem pulverisierten Dentalfüllstoff-Farbgeber mit
einem gepulverten Peroxidhärter in einer Menge zwischen 0,05 Gew.-% und 0,7 Gew.-% des
Pulverbestandteiles besteht, und
(b) der Flüssigkeitsbestandteil im wesentlichen besteht aus:
(1) einem methacrylat-funktionellen Harz, das geeignet zur Verwendung in Dentalverbundstoff ist,
in einer Menge von 84-96 Gew.-% des Flüssigkeitsbestandteiles, und
50 (2) einem Photoinitiator für dieses Harz, bestehend aus einem Exciplex, der als ein Inhaltsstoff
entweder Ethyl-4-dimethylaminobenzoat oder Ethyl-2-dimethylaminobenzoat in einer Menge von
0,7 bis 10 Gew.-% des Flüssigkeitsbestandteiles einschließt, wobei der andere Inhaltsstoff
entweder 2,3-Borandion oder Benzil ist und in einer Menge von 0,01-8%, bezogen auf das
Gewicht des Flüssigkeitsbestandteiles vorliegt, bei einer Gesamtphotoinitiatormenge, in Gewicht
55 des Flüssigkeitsbestandteiles, von 0,7 bis 18%, wobei Pulver- und Flüssigkeitsbestandteile
geeignet sind, unmittelbar vor der Anwendung in einem Gewichtsverhältnis von 2:1 bis 3,5:1
Pulver zu Flüssigkeit zusammengemischt zu werden.

11. System nach Anspruch 10, worin der Pulverbestandteil in Gewicht des Pulverbestandteiles enthält:

	Bariumglas	23 - 30%
5	Lithiumaluminiumsilikat	54 - 70%
	Flintkieselerde	1 - 10%

bei einem Gesamtfüllstoffgehalt von etwa 97,5 bis 99,85%

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12. System nach Anspruch 10 oder 11, worin der Pulverbestandteil ebenfalls Essigsäure und gamma-Methacryloxypropyltrimethoxysilan enthält.

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13. System nach Anspruch 12, worin der Eisessig in einer Menge von 0,001 - 0,05 %, in Gewicht des Pulverbestandteiles, vorhanden ist, und das Silan in einer Menge von 0,1% bis 1,5%, in Gewicht des Pulverbestandteiles, vorhanden ist.

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14. System nach einem oder mehreren der Ansprüche 10-13, worin das Harz ethoxyliertes Bisphenol-A-dimethacrylat in einer Menge von 82 bis 99,3%, in Gewicht des Flüssigkeitsbestandteiles, ist.

15. System nach einem oder mehreren der Ansprüche 10-13, worin das Harz eine Mischung, in Gewicht des flüssigen Bestandteiles, von 60-84% ethoxyliertem Bisphenol-A-dimethacrylat und 40-16% Triethylenglycoldimethacrylat ist.

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16. System nach einem oder mehreren der Ansprüche 10-13, worin das Harz eine Mischung, in Gewicht des Flüssigkeitsbestandteiles, von 55% Bis-GMA und 36% Triethylenglycoldimethacrylat ist.

17. System nach einem oder mehreren der Ansprüche 10-16 unter Verwendung von 2,3-Bornandion in Mengen, in Gewicht des Flüssigkeitsbestandteiles, von 0,02-0,2%.

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18. System nach einem oder mehreren der Ansprüche 10-17, worin der Flüssigkeitsbestandteil ebenfalls BHT (butyliertes Hydroxytoluol) in einer Menge von 0,02 %, in Gewicht des Flüssigkeitsbestandteiles, einschließt.

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19. Zweipastensystem nach Anspruch 1 für Porzellan- und Dentalreparatur, wobei diese Pasten geeignet sind, zum Zeitpunkt der Anwendung in praktisch gleichen Gewichtsmengen zusammengemischt zu werden, wobei beide Pasten methacrylat-funktionelles Harz mit der Eignung zur Verwendung in Dentalkomponenten und Dentalfüllstoffmaterialien in einer Gesamtmenge oberhalb 95% in Gewicht jeder Paste hiervon enthalten.

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20. System nach Anspruch 19, wobei jede Paste ebenfalls gamma-Methacryloxypropyltrimethoxysilan in einer Menge von 0,06 bis 1,2% in Gewicht jeder Paste enthält.

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21. System nach Anspruch 20, bei welchem wenigstens eine der Pasten weiterhin Eisessig in einer Menge von wenigstens 0,0015% in Gewicht dieser Paste enthält.

22. System nach einem oder mehreren der Ansprüche 19-21, worin das Harz ethoxyliertes Bisphenol-A-dimethacrylat ist.

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23. System nach einem oder mehreren der Ansprüche 19-22, worin jedes Harz in der peroxidhaltigen Paste in einer Menge von 14-40% vorhanden ist und in der den Exciplex enthaltenen Paste in einer Menge von 14-36% vorhanden ist.

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24. System nach einem oder mehreren der Ansprüche 19-23, worin der Füllstoff ausgewählt ist aus (a) Strontiumglas und einer Mischung von Bariumglas mit Lithiumaluminiumsilikat und weiterhin pyrogene Kieselsäure enthält.

25. System nach Anspruch 24, worin der Füllstoff in Gewicht einer jeden Paste etwa 1% an pyrogener Kieselsäure und etwa 80% an Strontiumglas umfaßt.
- 5 26. System nach Anspruch 24, worin der Füllstoff in Gewicht einer jeden Paste etwa 1% an pyrogener Kieselsäure, 24% Bariumglas und 56-57% an Lithiumaluminiumsilikat umfaßt.
27. Pasten-Pulver-system nach Anspruch 1 zur Verwendung bei Zahn- und Porzellanwiederherstellung, wobei die Paste und das Pulver geeignet zum Vermischen am Zeitpunkt der Anwendung in einem Verhältnis von Paste zu Pulver von 10:1 bis 20:1 geeignet sind,
10 wobei die Paste das Gemisch aus methacrylat-funktionellem Dentalharz und gepulvertem Dentalfüllstoff in einer zwischen 96-98%, in Gewicht der Paste, liegenden Gesamtmenge umfaßt und einen gegenüber sichtbarem Licht reaktionsfähigen Exciplex-Photoinitiator aufweist, wobei das Pulver im wesentlichen aus einem Dentalfüllstoff und einem Peroxidhärter für das Harz in einer Menge von 0,3%-10% des Pulvers besteht,
15 wobei der Exciplex angesetzt ist aus
(a) 2,3-Bornandion in einer Menge von etwa 0,03% bis 0,06%, in Gewicht dieser Paste, und
(b) entweder Ethyl-4-dimethylaminobenzoat oder Ethyl-2-dimethylaminobenzoat in einer Menge von etwa 0,75 bis 3,25% in Gewicht dieser Paste.
- 20 28. System nach einem der Ansprüche 1, 10 und 27, worin das Harz ausgewählt ist aus ethoxyliertem Bisphenol-A-dimethacrylat, Bis-GMA, einer Mischung hiervon mit einem Ethylenglycoldimethacrylat, und einer Mischung aus Bis-GMA mit einem Ethylenglycoldimethacrylat.
29. System nach Anspruch 27, worin das Harz 16-63,4%, in Gewicht dieser Paste, ethoxyliertes Bisphenol-A-dimethacrylat ist.
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30. System nach Anspruch 27, worin das Harz eine Mischung aus 13% ethoxyliertem Bisphenol-A-dimethacrylat und 3,25% Triethylenglycoldimethacrylat, jeweils in Gewicht dieser Paste, ist.
- 30 31. System nach Anspruch 17, worin das Harz eine Mischung aus 10% Bis-GMA und 6,5% Triethylenglycoldimethacrylat, jeweils in Gewicht dieser Paste, ist.
32. System nach Anspruch 27, worin wenigstens das Pulver gamma-Methacryloxypropyltrimethoxysilan in einer Menge von 1,25 bis 5,25% in Gewicht seines Bestandteiles enthält.
- 35 33. System nach Anspruch 27 oder 32, worin wenigstens das Pulver Eisessig in einer Menge von 0,02 bis 0,17%, in Gewicht seines Bestandteiles, enthält.
34. Gel-Pulver-system nach Anspruch 1 zur Verwendung bei der Zahn- und Porzellanwiederherstellung,
40 wobei das Gel und das Pulver zum Vermischen zum Zeitpunkt der Verwendung zum Aushärten durch sichtbares Licht in einem Verhältnis von 20:1 bis 1:3 des Gels zu dem Pulver geeignet sind, wobei das Gel im wesentlichen aus etwa 3/4 methacrylatfunktionellem Dentalharz und etwa 1/4 Dentalfüllstoff zu einer Menge von 90,7-98% in Gewicht dieses Gels und einem gegenüber sichtbarem Licht reaktiven Exciplex-Photoinitiator mit den beiden Bestandteilen (a) und (b) besteht,
45 wobei das Pulver im wesentlichen aus einem Dentalfüllstoff und einem beschleunigerfreien Peroxidhärter für das Harz in einer Menge von 0,05-4,69% in Gewicht dieses Pulvers besteht, wobei der Photoinitiator hergestellt ist aus:
(a) 2,3-Bornandion in einer Menge von 0,005 bis 0,15% in Gewicht dieses Gels, und
(b) entweder Ethyl-4-dimethylaminobenzoat oder Ethyl-2-dimethylaminobenzoat in einer Menge von
50 etwa 2,0 bis 8% in Gewicht dieses Gels.
35. System nach Anspruch 34, worin dieses Harz ethoxyliertes Bisphenol-A-dimethacrylat ist.
36. System nach Anspruch 10 oder Anspruch 34, worin dieser Füllstoff für den Pulverbestandteil ausgewählt ist aus: Bariumglas, Strontiumglas, Lithiumaluminiumsilikat, Flintkieselerde und Mischungen von Mitgliedern dieser Gruppe mit allen anderen.
55
37. System nach Anspruch 34, worin der Füllstoff für den Pulverbestandteil eine Mischung aus Bariumglas,

Lithiumaluminiumsilikat und Flintkieselerde ist.

38. System nach Anspruch 37, worin der Füllstoff für den Pulverbestandteil in Gewicht des Pulvers enthält: 23-30% Bariumglas, 54-70% Lithiumaluminiumsilikat und 1-10% Flintkieselerde.
39. System nach Anspruch 27 oder 34, worin der Füllstoff für den Gelbestandteil pyrogene Kieselsäure ist.
40. System nach Anspruch 27 oder 34, worin der Füllstoff für den Gelbestandteil eine Mischung von Bariumglas und Lithiumaluminiumsilikat umfaßt.
41. System nach Anspruch 34, worin der Füllstoff für den Gelbestandteil in Gewicht des Gels umfaßt: 2-5% Bariumglas, 5-10% Lithiumaluminiumsilikat und 7-10% pyrogene Kieselsäure.
42. System nach Anspruch 34, worin wenigstens der Pulverbestandteil gamma-Methacryloxypropyltrimethoxysilan in einer Menge von 0,05 bis 1,5% in Gewicht seines Bestandteiles enthält.
43. System nach Anspruch 34, worin wenigstens der Gelbestandteil Eisessig in einer Menge von etwa 0,01 bis 0,05% in Gewicht seines Bestandteiles enthält.
44. Verfahren zur Reparatur von Porzellan oder Zähnen mit Hilfe eines Zweikomponentensystems, wobei das Verfahren folgende Stufen umfaßt:
Zusammenmischen unter gewöhnlichen Innenbeleuchtungsbedingungen:
- eines methacrylat-funktionellen Harzes, das in Dentalverbundstoffen brauchbar ist, und eines Photoinitiators für dieses Harz, wobei der Photoinitiator ein Exciplex von (1) entweder 2,3-Bornandion oder Benzil und (2) entweder Ethyl-4-dimethylaminobenzoat oder Ethyl-2-dimethylaminobenzoat ist (Komponente 1), und
 - einem pulverförmigen Dentalfüllstoff-Farbgeber und wenigstens einem beschleunigerfreien Peroxidhärter für dieses Harz (Komponente 2), wobei das Zweikomponentensystem sein kann:
 - (a) ein Pasten-Pasten-system
 - (b) ein Pasten-Pulver-system,
 - (c) ein Gel-Pulver-system oder
 - (d) ein Flüssigkeits-Pulver-system, wobei der Photoinitiator, der Peroxidhärter und die ersten und zweiten Komponenten in diesen Systemen in Mengen vorliegen von:

System	Photoinitiator		Peroxid-härter		Kompo- .Kompo- nente 1 :nente 2	
		Gew.-%		Gew.-%		
(a)	1,50-3,50	Gew.-%	0,10-0,75	Gew.-%	1	: 1
(b)	0,70-3,70	Gew.-%	0,30-10,00	Gew.-%	20:1	- 10:1
(c)	2,00-8,00	Gew.-%	0,05-4,69	Gew.-%	20:1	- 1:3
(d)	0,70-18,00	Gew.-%	0,05-0,70	Gew.-%	1:1	- 1:4

wobei die Prozentsätze sich auf die Bestandteile dieser Komponente des Systems, welche die jeweilige Verbindung enthalten, beziehen;

Anbringen der Mischung innerhalb weniger Minuten nach dem Mischen und Aushärten eines wesentlichen Teiles der an Ort und Stelle angebrachten Mischung in situ für eine halbe Minute unter intensiver Beleuchtung mit sichtbarem Licht mit wenigstens 53800 lx (5000 foot candles), wobei beliebiges dann durch das Licht nicht ausgehärteter Harz innerhalb der nächsten Stunde durch den Peroxidhärter ausgehärtet wird,
mit der Ausnahme derjenigen Methoden, welche in den Rahmen des Art. 52(4) EPC fallen.

45. Verfahren nach Anspruch 44, bei welchem das Harz wenigstens ein Harz ist, das ausgewählt ist aus ethoxyliertem Bisphenol-A-dimethacrylat, Bis-GMA und einem Addukt von 2,2'-Propan-bis-[3-(4-phenoxy)-1,2-dihydroxypropan-1-methacrylat] und Mono- oder Diisocyanat.

46. Verfahren nach Anspruch 44 unter Verwendung eines Flüssigkeits-Pulver-systems, bei welchem der Exciplex 0,7% bis 18%, in Gewicht dieser Flüssigkeitsmischung, darstellt, und wobei das Peroxid etwa 0,05 bis etwa 0,7% der Pulvermischung darstellt.
- 5 47. Verfahren nach Anspruch 44 unter Verwendung eines Flüssigkeits-Pulver-systems, bei welchem zwischen dem Herstellen und Mischen die Stufe der Lagerung dieses Pulvers in einem Behälter und der Lagerung der Flüssigkeit in einem opaken Behälter vorhanden ist.
- 10 48. Verfahren nach Anspruch 44 unter Verwendung eines Pasten-Pasten-systems, worin wenigstens die erste Paste lange vorher hergestellt ist und die Stufe der Lagerung dieser ersten Paste in einem opaken Behälter bis zu dieser Mischstufe umfaßt.
49. Verfahren nach Anspruch 44 unter Verwendung eines Pasten-Pasten-systems, bei welchem dieser Exciplex 1,5 bis 3,5% in Gewicht der ersten Paste darstellt, und wobei dieses Peroxid 0,1 bis 0,75% in
15 Gewicht dieser zweiten Paste darstellt.
50. Verfahren nach Anspruch 44 unter Verwendung eines Pasten-Pulver-systems, worin das Vermischen der Paste weit vor der Verwendung einschließlich der Stufe der Lagerung dieser Paste in einem opaken Behälter durchgeführt wird, bevor das Pulver mit der Paste vermischt wird.
20
51. Verfahren nach Anspruch 44 unter Verwendung eines Pasten-Pulver-systems, worin der Exciplex 0,7 bis 3,7% der Paste darstellt und wobei das Peroxid 0,3 bis 10% dieses Pulvers darstellt.
- 25 52. Verfahren nach Anspruch 44 unter Verwendung eines Gel-Pulver-systems, wobei das Verfahren umfaßt: das Miteinander-Vermischen unter gewöhnlichen Innenbeleuchtungsbedingungen von einem Gel, bestehend im wesentlichen aus etwa 3/4 methacrylat-funktionellem Dentalharz und etwa 1/4 Dentalfüllstoff zu einer Gesamtmenge von 90,7 bis 98% in Gewicht des Gels und eines gegenüber sichtbarem Licht reaktionsfähigen Exciplex-Photoinitiator mit zwei Inhaltsstoffen, wovon einer ist:
30 (a) 2,3-Bornandion in einer Menge von 0,005 bis 0,15% in Gewicht, und
der andere ist:
(b) Ethyl-4-dimethylaminobenzoat oder Ethyl-2-dimethylaminobenzoat in einer Gesamtmenge von etwa 2% bis 8% in Gewicht des Gels, mit einem Pulver, bestehend im wesentlichen aus einem Füllstoff und einem beschleunigerfreien Peroxidhärter für das Harz in einer Menge von 0,05-4,69% in Gewicht des Pulvers, bei einem Verhältnis von 20:1 bis 1:3 des Gels zum Pulver.
35
53. Verfahren nach Anspruch 52, worin das Harz ethoxyliertes Bisphenol-A-dimethacrylat ist.
54. Verfahren nach Anspruch 52, worin der Füllstoff für den Gelbestandteil pyrogene Kieselsäure ist.
- 40 55. Verfahren nach Anspruch 52, worin der Füllstoff für den Gelbestandteil in Gewicht des Gels umfaßt: 2-5% Bariumglas, 5-10% Lithiumaluminiumsilikat und 7-10% pyrogene Kieselsäure.
56. Verfahren nach Anspruch 52, worin der Exciplex hergestellt ist aus
45 (a) entweder 2,3-Bornandion oder Benzil in einer Menge von 0,005 bis 0,15% in Gewicht des Gels, und
(b) entweder Ethyl-4-dimethylaminobenzoat oder Ethyl-2-dimethylaminobenzoat in einer Menge von 2,0 bis 7,5% in Gewicht des Gels.
57. Verfahren nach Anspruch 52, worin der Füllstoff für den Pulverbestandteil ausgewählt ist aus: Bariumglas, Lithiumaluminiumsilikat, Flintkieselerde und Mischungen der Mitglieder dieser Gruppe untereinander.
50
58. Verfahren nach Anspruch 52, worin der Füllstoff für den Pulverbestandteil in Gewicht des Pulvers enthält: 23-30% Bariumglas, 54-70% Lithiumaluminiumsilikat und 1-10% Flintkieselerde.
55
59. Verfahren zur Herstellung einer lagerfähigen, Zweikomponenten-Füllstoffharzmasse zur Verwendung bei der Porzellanreparatur und als Dentalverbundstoff, umfassend:
zur Herstellung der zweiten Komponente, das Übersichten eines pulverförmigen Dentalfüllstoffes mit

wenigstens einem beschleunigerfreien Peroxidhärter für das Harz,

Lagern dieses Füllstoffes;

zur Herstellung der ersten Komponente, das Vermischen eines nicht ausgehärteten methacrylat-funktionellen Harzes, das in Dentalverbundstoffen brauchbar ist, mit Photoinitiator für dieses Harz, wobei der Photoinitiator ein Exciplex von (1) entweder 2,3-Bornandion oder Benzil und (2) entweder

Ethyl-4-dimethylaminobenzoat oder Ethyl-2-dimethylaminobenzoat ist,

Lagern der Harz-Photoinitiatormischung in einem opaken Behälter,

wobei das Zweikomponentensystem ist entweder:

(a) ein Pasten-Pasten-system,

(b) ein Pasten-Pulver-system,

(c) ein Gel-Pulver-system oder

(d) ein Flüssigkeits-Pulver-system, wobei der Photoinitiator, der Peroxidhärter und die ersten und zweiten Komponenten in diesen Systemen in Mengen vorhanden sind von:

System	Photoinitiator		Peroxid-härter		Kompo- nente 1	Kompo- nente 2
(a)	1,50-3,50	Gew.-%	0,10-0,75	Gew.-%	1	1
(b)	0,70-3,70	Gew.-%	0,30-10,00	Gew.-%	20:1	10:1
(c)	2,00-8,00	Gew.-%	0,05-4,69	Gew.-%	20:1	1:3
(d)	0,70-18,00	Gew.-%	0,05-0,70	Gew.-%	1:1	1:4

wobei die Prozentsätze auf die Bestandteile dieser Komponente des Systems, welche die jeweilige Verbindung enthält, bezogen sind.

60. System oder Verfahren nach einem der vorhergehenden Ansprüche, bei welchem der Peroxidhärter Benzoylperoxid ist.